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A STUDY OF THE FORMS IN WHICH SULPHUR OCCURS IN COAL

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BY

R. POWELL

WITH

S. W. PARR

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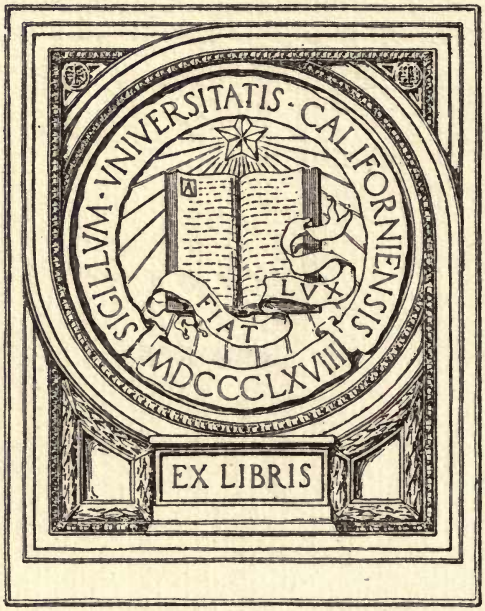

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A STUDY OF THE FORMS IN WHICH SULPHUR OCCURS IN COAL

BY

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ERRATA

Page 6, line eight: *for* "as pyrites, or marcasite sulphates," *read* "as pyrites o marcasite, sulphates."

Page 35, line nine: *for* "sulphuric" *read* "sulphinic".

Page 60, line eighteen: *for* "E. F. Charlton" *read* "E. E. Charlton."

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A STUDY OF THE FORMS IN WHICH SULPHUR OCCURS IN COAL

I. Introduction

1. *Present Status of Knowledge of Sulphur in Coal.*—Although carbon, hydrogen, and oxygen are generally considered to be the three important elements in coal, sulphur often forms a large portion of the coal substance.* In Illinois coals the sulphur often weighs as much or more than the quantity of hydrogen, but the behavior of these substances is radically different. The heat value of sulphur, for example, is less than one-twelfth that of hydrogen. The products of combustion moreover differ widely, the sulphur burning to an acid and the hydrogen to water. Other marked differences occur in the processes of combustion and of coking. These differences are modified to a certain extent by the original forms in which the sulphur occurs in the coal substance. From these considerations it is obvious that a knowledge of sulphur in its initial forms in coal is highly desirable.

For some time sulphur in coal has been known to be combined with iron as iron pyrites and marcasite, both of which have the formula FeS_2. Very small quantities of sulphates also are found, but the amount is so small, especially in freshly mined coal, that it is almost negligible. Free sulphur has been suspected to be present in coal, but its presence is the exception rather than the rule. Iron pyrites is undoubtedly the chief inorganic sulphur compound found in any great quantity in coal.

There are many indications that organic sulphur compounds form a large part of the sulphur in coal, but the nature of these compounds or the amount of sulphur so combined has never been determined prior to this investigation. Since the organic sulphur had its source in the protein sulphur of the plant and animal life from which the coal was formed, it is probable that these compounds in the coal are degradation products of the original material.

Methods† for the analysis of the total sulphur of coal are numerous and need not be described here. They all depend upon the general

*See Appendix I for a historical discussion of the constitution of coal.

†See Appendix II for a historical discussion of the development of a method for analyzing the forms of sulphur in coal.

principle of completely oxidizing the sulphur to the sulphate form and then precipitating it as barium sulphate. No reliable and accurate method, however, has been devised for estimating each form of sulphur in coal. The method generally used at the present time is indirect and makes use of the following assumptions. All the sulphur in coal is assumed to be present as pyrites, or marcasite sulphates, and organic sulphur. The amount of sulphate sulphur is estimated by dilute hydrochloric acid extraction. In addition to the determination of sulphate sulphur in the extract, the iron is also determined. The remainder of the iron in the coal, which is obtained by subtracting the extract iron from the total iron, is assumed to be combined with sulphur to form pyrites. By a simple stoichiometrical calculation the pyritic sulphur may be determined. Since only three forms of sulphur were assumed to be present, the organic sulphur content is calculated by subtracting the amount of the two inorganic forms from the total sulphur.

Investigations prove that coal undergoes considerable oxidation while in storage, to some extent when it is in free contact with the air, but to a less extent when it is stored in air tight containers. The oxidation of the coal substance as a whole includes the oxidation of the sulphur in coal. The iron pyrites oxidizes to the sulphate form so that whereas fresh coal generally contains only a trace of sulphates, coal after being stored two or three years may have the major portion of the inorganic sulphur present as sulphate.

When coal is subjected to destructive distillation not in contact with air, the sulphur present divides between the residue and the volatile matter. The ratio between the residual sulphur and the volatile sulphur in coal varies between wide limits. It remains fairly constant, however, for the same coal. The factors which control this ratio are not yet determined except in a very general manner. Certain coal constituents, entirely separate from the sulphur containing compounds, may have an effect on the percentage of sulphur retained in the coke, but in all probability the decisive factor affecting the sulphur content is the relative amounts of the different sulphur forms present.

The sulphur in the volatile matter resulting from the destructive distillation of coal is in the form of hydrogen sulphide or thiophen derivatives, but the nature of the sulphur retained in the coke has never been fully determined. A portion of it is known to be present in the form of sulphides, but the larger part seems to exist in organic combination.

2. *Purpose of the Proposed Study.*—The purpose of this investigation has been to make a thorough study of the nature of the sulphur containing compounds in coal, the quantity of each form present, and the change which characteristic forms undergo when the coal is allowed to stand or is subjected to coking. It has been stated that coal was assumed to contain three types of sulphur compounds. The present investigation was undertaken to prove or disprove the presence of these types, to find out if other types exist and to devise methods for the quantitative study of each form.

With this preliminary work as a background, the changes which the sulphur in coal underwent through oxidation and the factors entering into these changes were then studied. The question of pyrites as a cause of spontaneous combustion in coal and the question of the deterioration of heating value are closely connected with the oxidation of sulphur in coal. For this reason a study of some of the conditions governing the phenomenon was of practical importance.

A practical application of the sulphur in coal study is the coking of coal. The purpose of this investigation was not only to determine some relationship between the amounts of the various sulphur forms in coal and the residual sulphur left in coke, but also to determine the nature of the sulphur retained in the coke. A knowledge of these conditions would be at least one step toward a means for controlling the sulphur content of coke.

3. *Conclusions.*—A study of the data contained hereinafter suggests the following conclusions:

(1) The sulphur of coal occurs in four characteristic forms, two of them organic and two inorganic.

(a) If the resinic organic type is shown to be organic sulphur by its lack of an ash, its presence in that portion of the organic material soluble in phenol indicates its association with that substance.

(b) The humus organic sulphur is shown to be organic by the very small amount of ash in the compounds in which it occurs. These compounds are shown to be closely related to humus substances by their chemical action.

(c) The pyritic or marcasitic sulphur is present as FeS_2 as indicated by the iron-sulphur ratio when the pyrites is oxidized and taken into solution.

(d) The sulphate sulphur is shown to be such by the fact that it dissolves in dilute hydrochloric acid as sulphate without preliminary oxidation.

All four forms have therefore been definitely proved present, and only these forms exist in the coal since the combined percentages account for all the sulphur. Free sulphur was not found in any of the samples of coal and is presumably absent except in unusual cases where it might occur in small quantities as a decomposition product of pyrites.

(2) The early method of determining the forms of sulphur in coal gives high results for the pyritic sulphur and low results for the organic sulphur. The method developed in this investigation is decidedly more nearly accurate for the analysis of the different forms of sulphur in coal.

(3) Some of the sulphur in coal, probably in the form of iron pyrites, is oxidized gradually to the form of sulphate. One of the chief factors in this reaction seems to be the length of time of standing. An excess of air has no very decisive effect upon oxidation; in fact, coal kept in a tightly stoppered flask oxidizes freely.

(4) The reaction seems to be hastened by the presence of bacteria or some catalytic agent. This influence is not evident at first, probably because of the large amount of free oxygen present in the flask.

(5) The amount of soluble sulphate formed by the reaction is less than it would be if the amount of soluble iron is taken as a criterion. This fact suggests the union of some of the oxidized sulphur with the organic matter of the coal.

(6) It seems probable from this investigation that when the coal is coked the sulphur forms of the coals change as follows:

(a) The sulphate sulphur is retained by the coke but in some form other than inorganic sulphate.

(b) The pyritic sulphur is partially volatilized and a portion is also left in the coke, probably as sulphide sulphur. All the pyrites is decomposed.

(c) Most of the resinic sulphur is left in the coke, but in a form different from that existing in the coal.

(d) The humus sulphur volatilizes partly but some is left in the coke in a changed form.

(7) The forms of sulphur in the coke were studied, but they were not fully identified. A small part of the sulphur exists as sulphide, and the remainder is probably in combination with carbon. This last form is extremely stable to strong acids, oxidizing agents and heat, but readily gives up its sulphur as hydrogen sulphide when subjected to the action of nascent hydrogen.

(8) During the coking process, secondary reactions between constituents of the coal and decomposed sulphur compounds affect the quantity of sulphur retained by the coke.

II. The Development of a Method for Analyzing the Different Forms of Sulphur in Coal*

4. *The Method Involving the Use of Organic Solvents.*—The first method used to determine the different forms of sulphur in coal was that of organic solvents for removing the organic compounds with the idea that possibly all the organic sulphur would be acted upon by the solvent employed and would be found in the extract.

The solvent which extracted the greatest amount of material was phenol. In a few cases, the amount of sulphur in this extracted material was determined, but since this was both a difficult and time-consuming procedure only the insoluble residue was analyzed for its sulphur content. The difference between the amount found and the total sulphur was the sulphur in the extract. It is seen that this procedure calls for the determination of the total sulphur. If in that connection the total iron is also determined, the assumption may be made that all the inorganic sulphur is combined with the iron either as FeS_2 or $FeSO_4$. If this assumption is correct, all the factors necessary for determining the various forms of sulphur present, namely, the total sulphur, the inorganic sulphur as sulphate and pyrites and by difference, the organic sulphur, might be found in the phenol soluble extract or divided between that material and the cellulosic or insoluble residue.

This method for determining the different sulphur forms was provisional and had no exact experimental confirmation but was regarded as the best method available at the time. The analytical procedure was as follows. The percentage of all constituents was based upon the coal as weighed out for analysis. A sample of coal was obtained, together with any information concerning where and how recently it had been mined and any other facts which seemed pertinent to the investigation. No effort was made to get representative samples, since a study of the compounds in one piece of coal would give results similar to those of a mixed sample, as far as the general composition of the coal and a method of analysis were concerned. This sample was then ground to about pea size by a rotary crusher; then the coal was spread out in a thin layer for several hours to secure in the sample the moisture conditions of the room. It was then ground to 100-mesh size and stored in an air-tight container.

*See Appendix II for a historical account of the development of a method by other investigators.

A total sulphur and a total iron determination were made on a small quantity of the sample, and on a larger quantity a determination of the sulphur and the iron which were soluble in dilute hydrochloric acid. The percentage of total iron minus the percentage of hydrochloric-acid-soluble iron was considered to be the percentage of pyritic iron in the sample. From this result pyritic sulphur was estimated, it being assumed that pyrites always has the formula FeS_2. The sulphate sulphur was assumed to be that obtained in the hydrochloric acid extract. The organic sulphur was then taken as the difference between the total sulphur and the sum of the two inorganic forms.

The method used for determining the total sulphur and iron in the coal was that of Eschka and Fresenius. Although the results for the sulphur were fairly good, those for the iron were generally too low. A sodium peroxide fusion method, which gave excellent results, was then substituted; consequently this substitute method was used during the investigation for the analysis not only of the coal, but also for sulphur and iron in all residues.

This fusion was performed in a pure nickel crucible, having a loose fitting lid and a capacity approximating 50 cc. Some sodium peroxide was placed in the bottom, on top of which was placed the substance to be analyzed in the form of a fine powder. Sodium peroxide was then added until the crucible was about half full, the amount depending upon the quantity of coal substance used. With coal itself, half gram samples were used. The contents were thoroughly mixed by means of a glass stirring rod, and a thin layer of sodium peroxide was sprinkled over the top. The lid was put in position and held in place by a piece of metal weighing a few ounces. The charge was ignited by using a Bunsen burner to heat the outside of the crucible. Almost without exception, complete combustion of the organic matter occurred in a few seconds, without any of the charge blowing out under the lid. After the crucible had cooled somewhat, the fusion was dissolved out with water. The alkaline solution was carefully acidified with hydrochloric acid and filtered.

From this point in the analysis there was little variation from the ordinary methods of determining iron and sulphur in a solution. The hot solution was poured into a slight excess of ammonia and the mixture stirred to coagulate the ferric hydroxide. This hydroxide was filtered off and dissolved from the filter by using concentrated hydrochloric acid, and the amount of iron was determined by the usual Zimmermann-Reinhardt process. Since the quantities of iron were small in nearly

all cases, the potassium permanganate solution used was weak, its strength being about one-fortieth normal.

The filtrate from the ferric hydroxide was made slightly acid with hydrochloric acid. When it was brought to boiling 10 cc. of 10 per cent barium chloride were added slowly. The solution was heated and stirred for some time in order to prevent the passing of barium sulphate through the filter. Since this precipitate was small, a slight loss would cause a large percentage error. After filtering, the filter was ignited in a porcelain crucible and the barium sulphate weighed.

The method outlined in the preceding paragraphs varies in two particulars from the one ordinarily used. No oxidizing agent is added before precipitating the iron or the sulphur, since the sodium peroxide fusion has insured complete oxidation. A second precipitation of the iron to remove any basic sulphate is, furthermore, omitted, because the amount of precipitate as compared with the volume of the solution is so small. In order to show that a second precipitation was unnecessary and that the method used was accurate enough for the purposes of the investigation, the following experiment was performed. Two samples of pure ferrous ammonium sulphate were weighed out, one corresponding roughly to the sulphur content of one gram of a low sulphur coal, the other to that of a very high sulphur coal. The samples were dissolved in very dilute hydrochloric acid, oxidized by boiling with bromine water, and then run through the analysis just described. The results of this experiment are presented in Table 1.

TABLE I

CHECK ANALYSIS OF FERROUS AMMONIUM SULPHATE

Weight of sample	.0729 g.	.3080 g.
Theoretical per cent iron	14.3	14.3
Per cent iron determined	14.4	14.2
Theoretical per cent sulphur	16.4	16.4
Per cent sulphur determined	16.5	16.3

It will be noted that the variation between the theoretical and actual determination is very small. If larger samples had been used, the relative error would probably have been still smaller. Considering the error for the size of the samples of coal used, the error when using large samples would not be greater than 0.01 per cent. Since no conclusions are drawn within this amount, the method is suited to the conditions of the work.

The sulphur and the iron of coal soluble in dilute hydrochloric acid were determined from samples of the coal weighing 5 grams. These

samples were treated with 300 cc. of 3 per cent hydrochloric acid. This mixture was allowed to digest at 60 degrees Centigrade for 40 hours. The solution containing the soluble iron and sulphate sulphur was filtered off and oxidized by means of bromine water. Analyses were then made for both sulphur and iron by the method previously described. This method of extraction is accurate for the determination of sulphates. It does not determine other sulphur forms present, however, as shown by the fact that coals known to contain large quantities of pyritic and organic sulphur yielded no sulphur whatever by this means of extraction.

These methods when used as described will determine the percentage of the different forms of sulphur in coal, provided the assumptions previously made are correct.

The next step in the investigation, namely, the extraction of the coal with phenol, was made in a manner slightly different from that usually employed. Instead of dropping hot condensed phenol upon the coal in an extraction thimble, a flask containing both the finely powdered coal and the phenol was heated to 140 degrees Centigrade by an electric oven. A one-half gram of coal was placed in a 100 cc. Erlenmeyer flask. An air condenser about two feet long was placed in the neck of the flask with the condensing tube extending through the top. Twenty-five cubic centimeters of molten phenol were poured upon the coal. The flask was placed in the inner chamber of the electric oven and heated at a temperature of 140 degrees Centigrade for 20 hours, after which it was removed and the contents promptly filtered through a Gooch crucible. The flask was thoroughly rinsed with alcohol to remove any particles of residue and to dissolve the excess phenol from the residue in the crucible. An ether washing followed, the residue being allowed to dry in the crucible.

In a few cases, as mentioned in the foregoing, the extract was analyzed for its sulphur content, but the method was difficult and time-consuming. When such an analysis was made, the dark red extract was evaporated in a porcelain dish heated by the electric oven. When almost all the phenol had been driven off, the dish was allowed to cool and the remaining substance was carefully removed with a spatula. The substance was finely powdered and fused with sodium peroxide in order to get the sulphur into solution to analyze. To prevent the oxidation of the extracted substance while in the oven, a slow stream of carbon dioxide was passed through the heating chamber.

The most convenient way of determining both the residual and the

extracted sulphur, however, was the analysis of the insoluble residue. The residue was emptied from the Gooch crucible and mixed thoroughly with sodium peroxide. The analysis from this point was the same as that for the total sulphur in coal. Care had to be taken to make the asbestos mat as thin as possible, since the subsequent fusion with sodium peroxide took most of the asbestos into solution and trouble might be encountered later with the silicic acid when the barium sulphate was precipitated. With this precaution observed, the solution did not need to be evaporated to remove the silicic acid, since it does not precipitate with barium in dilute solutions.* The difference between this residual sulphur as thus determined and the total sulphur was the sulphur extracted by the phenol.

5. *Description of Apparatus Used.*—A cross-section of the electric oven especially constructed for the phenol solution experiments in this investigation is shown in Fig. 1. The cylindrical casing of galvanized iron was made 14 inches high and 12 inches in diameter. The inner chamber was a cylinder of heavy iron, 10 inches high and 5 inches in diameter, wrapped with asbestos paper and "nichrome" resistance wire in the form of a coil. Fifty feet of No. 20 wire was wrapped into a one-quarter-inch coil, doubled at the middle and coiled around the cylinder ten times so that the two ends came out at the top. On top of this wire a one-half-inch layer of fireclay-water glass mixture was placed, and the space between the inner chamber and the casing was filled with an asbestos-magnesia compound. An alternating current of 110 volts was used, and with no other resistance than the wire of the oven the current flowing was 3.1 amperes. In order to keep the temperature down to the 140 degrees desired, it was necessary to put lamps in the circuit for resistance.

In the experiments by Parr and Hadley on phenol extraction, an effort was made to exclude air from the extraction chamber by the use of a stream of carbon dioxide. The method used in the present investigation did not require this precaution as shown by the following experiment. Two flasks were used, one of which had the air condenser open at the top as usual. The other was closed by connecting it to a U tube containing alkaline pyrogallol. This U tube was attached to another containing water. The air was pumped from the flask and allowed to return through the two U tubes; thus only nitrogen was in the extraction

*Hillebrand, W. F., "Mineralogical Notes," U. S. Geological Survey, Bul. 167, p. 73, 1900.

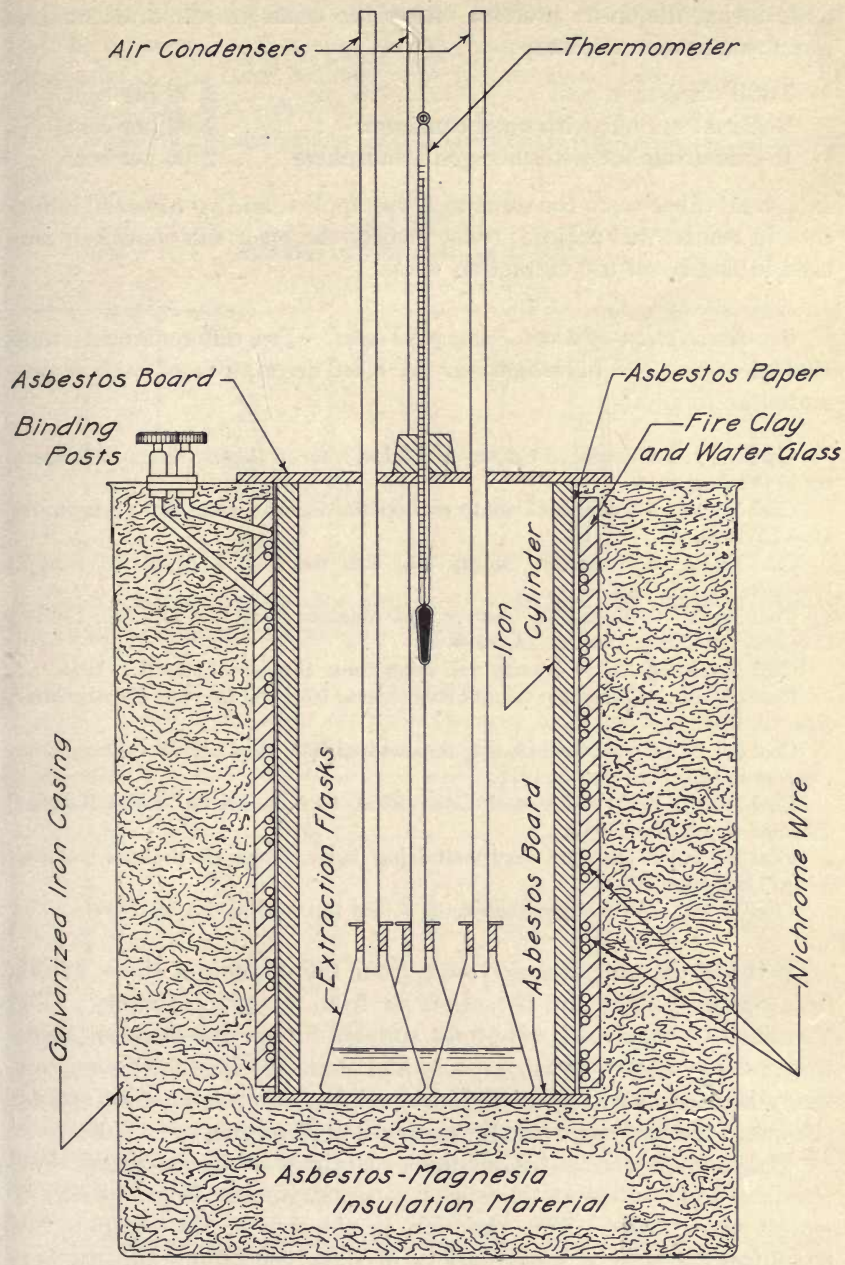

FIG. 1. CROSS-SECTION OF ELECTRIC FURNACE USED IN PHENOL EXTRACTION OF COAL

flask during the entire process. After the usual process of extraction these results were obtained:

Total sulphur in coal	2.18 per cent
Residual sulphur with open condenser	2.03 per cent
Residual sulphur with nitrogen atmosphere	2.06 per cent

In several other cases the same test was applied and no essential difference in results was noticed; consequently the open end condenser was used in nearly all the extraction work.

6. *Description of Coal Samples Tested.*—Ten different coals were studied during the investigation. A brief description of each is presented as follows:

Coal No. 1. A Vermilion County coal taken from an Illinois Traction Company car in October, 1915.

Coal No. 2. A Vermilion County coal obtained from a mine near Georgetown, May 19, 1915.

Coal No. 3. A Vermilion County coal collected from Kelly No. 4 mine at Westville, March, 1916.

Coal No. 4. A Vermilion County coal obtained from the Danville Colliery Company at Catlin, October 25, 1916.

Coal No. 5. A Saline County coal mined near Harrisburg, April 1, 1915.

Coal No. 6. A Vermilion County coal secured from the Danville Electric Mine, June 10, 1915.

Coal No. 7. A Vermilion County coal secured from the Danville Colliery Company at Catlin, February 3, 1917.

Coal No. 8. A Tennessee coal of the Jellico type, known as "Black Beauty," obtained about May, 1917.

Coal No. 9. A Japanese coal containing large clumps of resinous material, mined December, 1913.

Coal No.10. A Tennessee coal of the Jellico type obtained April 1, 1915.

Seven of the ten coals used were from Illinois, one of these coming from Saline County and the other six from Vermilion County. The Vermilion County coals were most suitable for the investigation, since their sulphur content was generally high and they contained comparatively large amounts of the different sulphur forms. Eastern anthracites were not analyzed since they contain little sulphur.

The samples were put in air-tight containers on the days they were obtained and studied at times over a period varying from one day to almost three years. The variation in the age of the samples was advantageous since a great variety of data concerning the sulphate

formed could be obtained. Sulphate sulphur, for example, increases rapidly in most coals during storage; consequently the hydrochloric-acid-soluble iron and sulphur were redetermined before each set of data on a coal was secured.

The proximate analysis of each of these coals is given in the following table.

TABLE 2

PROXIMATE ANALYSES OF COALS

(Values given in per cent)

Sample Number	Moisture	Volatile Matter	Fixed Carbon	Ash
1	6.77	41.37	43.48	8.38
2	4.26	34.24	45.29	16.21
3	11.37	35.85	47.83	4.95
4	5.98	42.82	45.90	5.30
5	4.72	34.73	54.29	6.26
6	5.54	38.36	40.13	15.97
7	2.69	42.81	45.05	9.45
8	1.63	37.39	58.22	2.76
9	2.05	44.47	42.40	11.08
10	3.53	35.97	59.54	0.96

The analyses for sulphur and iron on each of the coals, calculated on an air dry basis,* are given in Table 3.

TABLE 3

SULPHUR AND IRON CONTENT OF COALS

(Values given in per cent)

Sample Number	Total Sulphur	Total Iron	HCl sol. Sulphur	HCl sol. Iron
1	2.68	1.36	0.04	0.14
2	2.18	1.65	0.17	0.27
3	0.64	0.21	0.00	0.06
4	2.14	0.69	0.05	0.07
5	1.20	0.55	0.25	0.20
6	5.00	3.40	1.31	1.62
7	3.31	1.87	0.01	0.07
8	1.02	0.82	0.01	0.12
9	1.40	0.95	0.02	0.29
10	0.94	0.38	0.02	0.11

In this table an effort has been made to show the percentage of hydrochloric-acid-soluble sulphur and iron when the phenol extraction was made. As previously mentioned, these values change somewhat rapidly; so this determination was repeated at intervals during the progress of the investigation.

*Unless otherwise stated, all percentages through the investigation are referred to the basis of the air dried coal.

7. *Results Obtained by Organic Solvent Methods.*—Table 4 gives the results of phenol extraction of these coals and a comparison with the organic and inorganic forms of sulphur in the coal as calculated from the foregoing data. The method used in calculating these forms of sulphur has been indicated, but it may be repeated in a more definite manner. The pyritic sulphur, that is, the sulphur combined as iron pyrites or marcasite, was deduced by subtracting the soluble iron from the total iron and then multiplying this result by 1.145 which is the chemical factor for calculating the equivalent of sulphur combined with the iron when the two are associated as pyrite. The sulphate sulphur was considered the same as the soluble sulphur.

TABLE 4

COMPARISON OF SULPHUR EXTRACTED BY PHENOL WITH ORGANIC SULPHUR

(Values given in per cent)

Sample Number	A Total Sulphur	B Sulphur as FeS_2	C Sulphur as Sulphate	D Total Organic S by Difference, i. e., A—(B+C)	E Organic S: Soluble in Phenol	F Difference between Total Organic S and Phenol Soluble S
1	2.68	1.39	0.04	1.25	0.42	0.83
2	2.18	1.58	0.17	0.43	0.15	0.28
3	0.64	0.17	0.00	0.47	0.20	0.27
4	2.14	0.71	0.05	1.38	0.34	1.04
5	1.20	0.40	0.25	0.55	0.16	0.39
6	5.00	2.03	1.31	1.66	0.77	0.89
7	3.31	2.06	0.01	1.24	0.50	0.74
8	1.02	0.80	0.01	0.21	0.10	0.11
9	1.40	0.75	0.02	0.63	0.21	0.42
10	0.94	0.31	0.02	0.61	0.12	0.49

It may easily be seen from this table of experimental results that no relationship whatever exists between the amount of sulphur extracted by the phenol and the amount calculated to be present as organic sulphur, except that the latter is always considerably larger than the former. This difference in results may be due to any one of several conditions. The phenol may not extract all the organic sulphur compounds, or the sulphur may be present in some undetermined inorganic form. The standard of comparison has, moreover, not been definitely proved correct, for the iron considered to be pyritic iron may be combined with more sulphur than the theoretical amount for pyrite, or it may be combined with less sulphur as in coal which contains iron silicate.

A wide gap exists between the supposedly organic sulphur calculated by difference (column D) and the phenol soluble sulphur (column E)

which is known to be organic in character. That the phenol extracted sulphur is organic in nature cannot be doubted since the extract is practically ashless, and organic sulphur only must, therefore, be present. Two questions remain to be answered: first, is the iron, assumed to be combined as pyrites, quantitatively present as such, and secondly, what is the nature of that sulphur assumed to be organic and not extracted by phenol, the quantity of which is probably represented for each coal in the last column of Table 4?

To determine the nature of the sulphur assumed to be organic and not extracted by phenol, other solvent methods were used. Higher temperature or longer time than had been used for extraction by the phenol was not considered practicable according to previous research. As far as the amount of sulphur extracted was concerned, the method used in this investigation was as good or even better than the extraction thimble process of Parr and Hadley and of Charlton, as shown by a comparison of the two methods on the same coals. In every case the percentage of sulphur extracted by the phenol was slightly greater when determined by the method here described. Since no additional help could be obtained from phenol extractions of coal, other solvents were sought to extract the coal sulphur compounds.

Among these solvents pyridin and anilin have been used in a study of the constitution of coal. Since the amount of sulphur extracted by these solvents had not been investigated, some experiments of this nature seemed essential to the investigation; consequently a sample of coal No. 1 was extracted with pyridin and another with anilin. In these qualitative tests approximately the same amount of sulphur appeared in the extract as when phenol was used. These solvents, like phenol, had no effect on iron pyrites and calcium sulphate. In order to test them quantitatively, 0.5 gram samples of coals Nos. 1 and 3 were extracted with 25 cc. of anilin, the same method of procedure

TABLE 5

SULPHUR EXTRACTED BY ANILIN

(Values given in per cent)

Sample Number	Total Organic S by Difference	Organic S Soluble in Phenol	Organic S Soluble in Anilin	Difference between Total Organic S and Anilin Soluble S
1	1.25	0.42	0.44	0.81
3	0.47	0.20	0.09	0.38

being followed as with phenol. The temperature of the extraction was 140 degrees Centigrade. The results are given in Table 5.

Compared with the results obtained by the phenol extraction, the results are about the same for No. 1. For coal No. 3, however, they are not so good. No conclusions can be drawn from this experiment regarding the anilin soluble sulphur constituents being the same as those of the phenol soluble.

Another extraction experiment was tried in which a mixture of equal parts of phenol and aniline were used as the solvent. The conditions for this determination were the same as those for the preceding experiment. The following table gives the result.

TABLE 6

SULPHUR EXTRACTED BY PHENOL AND ANILIN

(Values given in per cent)

Sample Number	Total Organic S by Difference	Organic S Soluble in Phenol	Organic S Soluble in Phenol and Anilin	Difference between Total Organic S and Phenol-Anilin Soluble S
1	1.25	0.42	0.53	0.72

This experiment seemed to give better results than the preceding one, but the sulphur unaccounted for was still too great to regard this method as of practical value. Theoretically it was interesting, since it indicated that constituents might be extracted by the basic aniline different from those extracted by the acid-like phenol.

The extractions with pyridin had to be made at a temperature lower than that made with phenol and anilin, because of the lower boiling point of this solvent. The temperature chosen was 85 degrees Centigrade. The results are given in Table 7.

TABLE 7

SULPHUR EXTRACTED BY PYRIDIN

(Values given in per cent)

Sample Number	Total Organic S by Difference	Organic S Soluble in Phenol	Organic S Soluble in Pyridin	Difference between Total Organic S and Pyridin Soluble S
1	1.25	0.42	0.35	0.90
2	0.43	0.15	0.13	0.30

The sulphur extracted by pyridin is less than that removed by phenol; hence its use as a solvent was discarded. Benzene was tried as a solvent, but it also proved ineffective. From the experimental data given, the task of removing all the organic sulphur by means of an organic solvent seemed hopeless. Inorganic solvents were next used.

8. *Methods Involving the Use of Inorganic Solvents.*—The first inorganic solvent tried was sodium hydroxide. A sample, 0.5 g., of coal was extracted with phenol. The residue was then treated with 50 cc. of 5 per cent sodium hydroxide, allowed to stand at room temperature for 48 hours and filtered. The filtrate was then oxidized by means of sodium peroxide. An extraction of only 0.23 per cent of sulphur was secured from coal No. 1, having 0.83 per cent unaccounted for, and 0.39 per cent from coal No. 2 with 0.28 per cent unaccounted for. From these results it seemed evident that sodium hydroxide would not extract all the organic sulphur.

The second inorganic solvent tried was potassium permanganate, which according to qualitative tests has a noticeable solvent action on iron pyrite. It reacted also rather quickly on coal and took a quantity of sulphur into solution. The permanganate decolorized quickly in both cases and large quantities of manganese dioxide were precipitated. In no case, however, did the sulphur extracted by the permanganate approach in amount that of the pyritic sulphur, perhaps because of the ready reaction of the coal substance with the permanganate; hence repeated treatments were necessary to insure complete oxidation of the pyrites. Such discordant and inconclusive results were obtained and such large quantities of manganese dioxide were precipitated that this method was abandoned.

Concentrated nitric acid was the solvent next tried. This was known to be a complete solvent for the pyrites. Whether it would attack and take into solution the more stable organic sulphur compounds of the coal had to be determined. Gram samples of the coals were placed in beakers and covered with 25 cc. of concentrated nitric acid. After twenty-four hours of extraction, the percentages of sulphur given in Table 8 were found in the filtrate.

These results show that the nitric acid did not extract all the pyritic and sulphate sulphur as was assumed it would. The shortage might be attributed to extraction at room temperature. On the other hand the amount of calculated pyritic and sulphate sulphur may be high because

TABLE 8

CONCENTRATED NITRIC ACID EXTRACTION OF COAL

(Values given in per cent)

	Coal No. 1	Coal No. 2	Coal No. 4
Sulphur in HNO_3 Extract	1.20	1.47	0.41
Pyritic and Sulphate Sulphur as indicated from the iron present	1.43	1.75	0.76

of an incorrect assumption concerning the form in which the iron occurs. A negative result seems to be obtained in attempting to find if any of the organic sulphur was oxidized and taken into solution. At least the data in Table 8 indicate that scarcely any organic sulphur was affected.

All the experiments performed would tend to show that the sulphur unaccounted for is combined in an extremely stable form. The failure of nitric acid to extract all the pyritic and sulphate sulphur would particularly indicate this tendency. Free sulphur, however, might be left in the residue after the extraction with nitric acid. In order to determine this free sulphur the nitric acid treatment just described was repeated. The residue was then boiled with pure carbon tetrachloride to remove any possible free sulphur. The carbon tetrachloride was evaporated, and the slight residue left was mixed with benzoic acid and fused with sodium peroxide. This fusion was added to the nitric acid extract and the sulphur determined. By this modified method, the sulphur in the extract of coal No. 1 was raised 0.02 per cent and that of coal No. 2 raised 0.08 per cent. The formation of free sulphur during the nitric acid treatment accordingly seems of minor importance.

The only common inorganic substances which might conform to the conditions as thus given are certain sulphides and a few insoluble sulphates. After a sodium peroxide fusion of coal No. 4 was made, acidified with hydrochloric acid and passed in hydrogen sulphide, no precipitate except a little free sulphur was obtained. This experiment proved the absence of arsenic or any other metal which might make an insoluble sulphide. An excess of sulphuric acid was added to another portion of sodium peroxide fusion solution, but no precipitate was observed; thus the absence of metals forming insoluble sulphates was shown. By a process of elimination, therefore, it was essentially proved that the unknown sulphur of the coal was of some organic form, this fact being shown by experiments hereinafter described.

Although the concentrated nitric acid had proved a failure as a solvent for stable organic sulphur, it was an excellent solvent for the two inorganic forms, namely, the sulphate sulphur and the pyrites. The data given in Table 8 seemed to indicate that not all the pyritic sulphur was being extracted by the concentrated nitric acid. That all the pyrites was extracted and that the difference in percentages was due to false assumptions in the calculation of the pyritic sulphur will be shown later.

The method used in treating the coals with the concentrated acid was very simple. Twenty-five cubic centimeters of concentrated nitric acid were poured over one gram of coal and the mixture allowed to stand twenty-four hours before filtration and analysis of the extract. The results thus obtained are given in Table 9 together with the percentage of the combined pyritic and sulphate sulphur, as estimated by the old indirect method, and the total iron in the coal.

TABLE 9

CONCENTRATED NITRIC ACID EXTRACTION OF COAL

(Values given in per cent)

Sample Number	Sulphur in Acid Extract	Iron in Acid Extract	Pyritic Sulphur (as calculated from supposedly Pyritic Iron[1]) plus Sulphate Sulphur in Coal	Total Iron in Coal
7	1.72	1.53	2.07	1.87
7	1.76	1.52	2.07	1.87
7	1.77	1.51	2.07	1.87
7	1.72	....	2.07	....
7	1.77	....	2.07	....
7	1.69	....	2.07	....
4	0.65	0.62	0.76	0.69
4	0.65	0.58	0.76	0.69

If the method for calculating the pyritic sulphur as indicated from the iron present were correct, the two iron values and the two sulphur values should correspond, or the nitric acid extract sulphur percentage should be a little higher than the iron percentage because of partial oxidation of the organic sulphur. The calculated values, however, are all high as compared with those obtained directly.

Some doubt existed whether all the pyrites was being taken into solution by the nitric acid; consequently a series of experiments was begun to determine the effect of aqua regia on the coal. The method

[1]Pyritic Iron = Total Iron minus HCl Soluble Iron.

adopted was similar to that which made use of nitric acid, except that heat was applied to hasten the solution process, the time for which was reduced to about one hour. The solvent used consisted of one part of concentrated hydrochloric acid and three parts of concentrated nitric acid. Where only 0.65 per cent of sulphur had been extracted from coal No. 4 by means of nitric acid, the hydrochloric-nitric acid treatment yielded 0.74 per cent in a very short time, and 0.90 per cent during several hours on the water bath. Several coals were treated, and the results of these extractions are given in Table 10.

TABLE 10

HYDROCHLORIC-NITRIC ACID EXTRACTION OF COAL

(Values given in per cent)

Sample Number	Sulphur in Acid Extract	Iron in Acid Extract	Pyritic Sulphur (as calculated from supposedly Pyritic Iron[1]) plus Sulphate Sulphur in Coal	Total Iron in Coal
4	0.89	....	0.76	....
4	0.91	....	0.76	....
8	0.30	....	0.81	....
8	0.29	....	0.81	....
5	0.57	0.44	0.65	0.55
5	0.61	0.48	0.65	0.55
7	2.08	1.58	2.07	1.87
7	2.12	1.58	2.07	1.87
9	0.42	0.50	0.77	0.95
9	0.40	0.52	0.77	0.95
6	3.95	3.34	3.34	3.40
6	3.95	3.29	3.34	3.40

Several interesting conclusions may be drawn from this table of data. Without much doubt the strong solvent action of hot hydrochloric-nitric acid mixture established the presence of all the non-silicate iron in the filtrate. The silicate iron must then be considered the difference between the total iron and that in the filtrate. This difference is shown in the second and fourth columns of Table 10. In the case of coals Nos. 7 and 9, the amount of silicate iron is large. The error that this amount would cause in a pyritic sulphur determination by calculation from the iron present would be large. The data in Table 10 show that in some cases there is more sulphur in the extract than calculated to be present as pyritic and sulphate sulphur. Since the existence of silicate iron would reverse this discrepancy, the excess sulphur must be part of that organically combined, oxidized and taken into solution by the strong oxidizing solvent.

[1]Pyritic Iron = Total Iron minus HCl Soluble Iron.

As previously stated, the iron extracted by the acid mixture is almost certainly the non-silicate iron, or in other words the sum of the pyritic iron and the iron soluble in dilute hydrochloric acid. If from this sum the dilute acid soluble iron is subtracted, only the pyritic iron will be left and from this the exact amount of pyritic sulphur may be determined. Table 11 gives a comparison of the percentages of pyritic sulphur obtained by this method and by the method using the total iron minus the dilute acid soluble iron as representing the pyritic iron, and also gives the sulphur determined in the hydrochloric-nitric acid extract minus the sulphur soluble in dilute hydrochloric acid.

TABLE 11

COMPARISON OF PYRITIC SULPHUR DETERMINATIONS ON COALS BY DIFFERENT METHODS

(Values given in per cent)

	Coal No. 5	Coal No. 6	Coal No. 7	Coal No. 9
Pyritic S calculated from Pyritic Fe. (Pyritic Fe = HCl plus HNO_3 sol. Fe. minus dilute HCl sol. Fe.)	0.30	1.94	1.72	0.25
Pyritic S calculated from Pyritic Fe. (Pyritic Fe = Total Fe. minus dilute HCl sol. Fe)	0.40	2.03	2.06	0.75
Pyritic Sulphur by analysis (Pyritic S = HCl plus HNO_3 sol. S minus dilute HCl sol. S)	0.34	2.64	2.09	0.39

This comparison of results shows that both the amount of pyritic sulphur obtained by the older method of calculation from the total iron and the amount of pyritic sulphur obtained directly from the hydrochloric-nitric acid extraction are higher than that obtained by calculation from the iron soluble in hydrochloric-nitric acid. The high results of the method of calculation from the total iron are due to the presence of greater or less quantities of silicate iron, and the high results of the direct hydrochloric-nitric acid extraction of pyritic sulphur are due to the oxidation of a part of the organic sulphur. A method was sought to obviate the oxidation of this organic sulphur in order to determine the sulphur in the resultant extract directly as pyritic sulphur (plus the sulphate sulphur). The results produced would give separately the inorganic and organic forms of sulphur.

An experiment to make separate determinations of organic and inorganic sulphur by means of bromine was run on Coal No. 9,* but the results obtained were as unsatisfactory as those secured with the hydro-

*For a description of similar experiments by T. M. Drown see page 58.

chloric-nitric acid mixture. The bromine extraction apparently oxidized some of the organic sulphur as Ferdinand Fisher* found in his experiments.

A systematic search was conducted for a solvent which would dissolve the pyrites but not the organic sulphur. The plan followed is here briefly outlined. Samples of one of the analyzed coals were weighed out and extracted with dilute hydrochloric acid to remove all the sulphate sulphur and soluble iron. Sometimes the coal was also extracted with phenol; thus the resinic substances which appeared to oxidize rather readily under the action of oxidizing solvents were removed. Any solvent acting on this residue now took into solution only pyritic iron and sulphur either in the form of pyrites or organic sulphur, since these were the only possible forms remaining. Concentrated acid solvents acting on the residue for a long time would dissolve any silicate iron present, but the conditions were always such that they prevented dissolution. The next step was to treat the residue with the solvent for a stated length of time, filter, and analyze the filtrate for sulphur and iron. Since pyritic iron could be the only possible iron in the filtrate, the amount of pyritic sulphur may be calculated and compared with the sulphur actually in the filtrate. If these two values are the same and this relationship holds for different percentages of iron in the extract, only one conclusion is possible—that pyritic sulphur and only pyritic sulphur is being taken into solution.

The first experiment tried was preliminary and was a check determination using iron pyrites. A small quantity of finely powdered crystalline iron pyrites was mixed with some of coal No. 3. This coal was chosen because it had a very low sulphur content and would furnish the coal substance proper with very little organic sulphur. The sample was first extracted with dilute hydrochloric acid to remove all soluble iron and sulphur. The mixture now corresponded to a high sulphur coal, with nearly all the sulphur present as pyrites. One-half gram samples of this mixture were extracted with 15 cc. of hydrochloric-nitric acid mixture for a few minutes, diluted, filtered, and the filtrate analyzed for iron and sulphur. The results obtained, expressed in percentages of the original weight of the sample, are given in Table 12.

The different amounts of iron in the extracts result from the difference in activity of the beginning of the reactions, which were allowed to proceed for only a few minutes. These different amounts show that iron pyrites was extracted during every phase of the reaction. The

*See page 59.

TABLE 12

EXTRACTION OF COAL-IRON PYRITES MIXTURE WITH HYDROCHLORIC-NITRIC ACID

(Values given in per cent)

Sample Number	Iron in Acid Extract	Sulphur in Acid Extract	Pyritic Sulphur Calculated from Iron in Acid Extract as Pyritic Iron
1	1.67	1.94	1.91
2	1.34	1.53	1.53
3	1.30	1.44	1.48
4	1.30	1.51	1.48

similarity between the amount of sulphur in the acid extract and the amount as calculated from the iron in the acid extract leaves no doubt concerning this fact.

The next experiment was performed with coal No. 7. The effect of the hydrochloric-nitric acid treatment on this sample is shown in the following table. The extractions were allowed to proceed for different lengths of time; so varying quantities of pyrites would be extracted.

TABLE 13

EXTRACTION OF COAL NO. 7 WITH HYDROCHLORIC NITRIC ACID

(Values given in per cent)

Time of Extraction	Iron in Acid Extract	Sulphur in Acid Extract	Pyritic Sulphur Calculated from Iron in Acid Extract as Pyritic Iron
1 min.	0.30	0.37	0.34
2½ min.	0.53	0.76	0.61
5 min.	0.54	0.90	0.62
10 min.	0.77	1.32	0.88

This table shows experimental results already conjectured: viz., that so strong an oxidizing solution as hydrochloric-nitric acid not only attacks the pyrites but also oxidizes the organic sulphur. Attention is called to the increasing difference between corresponding figures in the last two columns as the time of extraction increases. This observation is evidence of the oxidation of sulphur other than that present in the pyritic form.

This relationship is expressed graphically by the series of curves shown in Fig. 2. The curve representing the sulphur in the acid extract rises much faster than the one showing the amount of sulphur calculated on the assumption that only pyrites is taken into solution. The lowest curve shows the amount of iron dissolved as a measure of the pyrites.

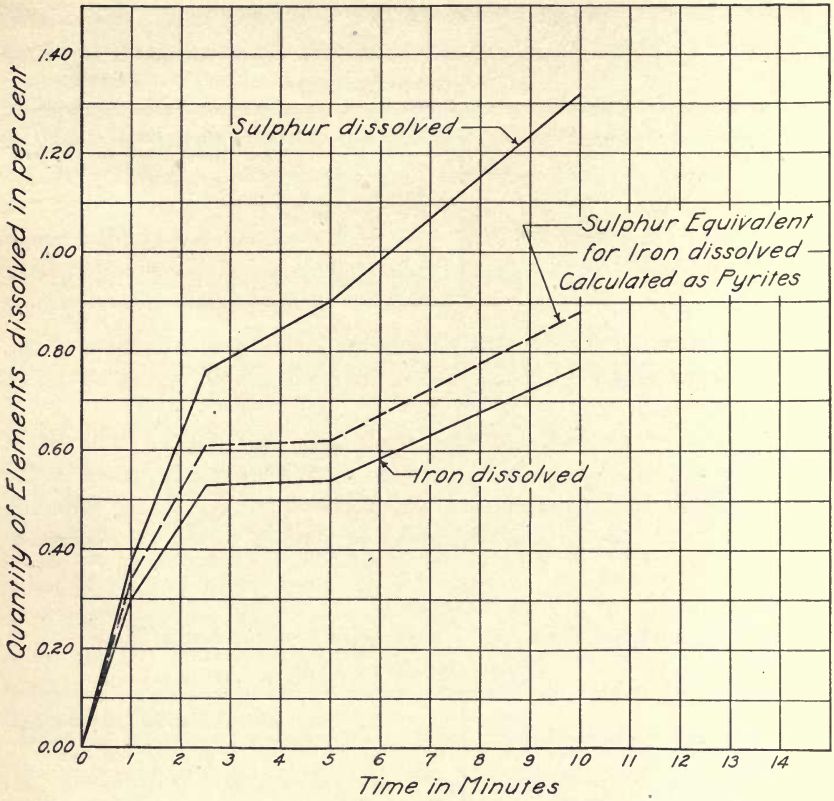

FIG. 2. CURVES SHOWING RESULTS OF THE EXTRACTION OF COAL NO. 7 WITH CONCENTRATED HYDROCHLORIC-NITRIC ACID

Table 14 shows the effect of concentrated nitric acid alone on coal No. 7.

TABLE 14

EXTRACTION OF COAL NO. 7 WITH CONCENTRATED NITRIC ACID

(One gram of coal used. Values given in per cent)

Time of Extraction	Iron in Acid Extract	Sulphur in Acid Extract	Pyritic Sulphur Calculated from Iron in Acid Extract as Pyritic Iron
2½ min.	0.90	1.05	1.03
5 min.	1.04	1.18	1.19
10 min.	1.05	1.16	1.20

These results make it appear that concentrated nitric acid is the most satisfactory solvent. Using two-gram samples of the coal, however, and allowing the extraction to proceed for a longer time gave the results shown in Table 15.

TABLE 15

EXTRACTION OF COAL NO. 7 WITH CONCENTRATED NITRIC ACID

(Two grams of coal used. Values given in per cent)

Time of Extraction	Iron in Acid Extract	Sulphur in Acid Extract	Pyritic Sulphur Calculated from Iron in Acid Extract as Pyritic Iron
1 min.	0.92	1.18	1.05
15 min.	1.01	1.35	1.15
30 min.	0.99	1.36	1.13
60 min.	1.00	1.36	1.14

These results indicate that concentrated nitric acid will attack the organic sulphur compounds as suggested by the difference between the corresponding figures in the last two columns; hence concentrated nitric acid does not make an ideal solvent for iron pyrites.

It was found convenient in such experiments to extract a quantity of coal with dilute hydrochloric acid* and then weigh out one-gram portions for each of the various solvent treatments, instead of extracting each sample separately. The analyses of some of these extracted coals are given in Table 16.

TABLE 16

SULPHUR AND IRON CONTENT OF COALS AFTER EXTRACTION WITH DILUTE HYDROCHLORIC ACID

(Values given in per cent)

Sample Number	Total Iron	Total Sulphur
5	0.44	1.08
6	2.22	4.00
7	1.62	3.13

In the following experiment, an effort was made to lessen the violent initial reaction between the nitric acid and the coal in order to reduce the action on the organic sulphur. The concentrated nitric acid was diluted with an equal volume of water and the solution was added to the coal when brought to a temperature considerably below that of the room. The results obtained with coal No. 6 are given in Table 17.

*Unless otherwise mentioned, it will be understood that this hydrochloric acid extracted material was used in all subsequent experiments. One-gram samples were generally used.

TABLE 17

EXTRACTION OF COAL NO. 6 WITH COLD NITRIC ACID

(Values given in per cent)

Time of Extraction	Iron in Acid Extract	Sulphur in Acid Extract	Pyritic Sulphur Calculated from Iron in Acid Extract as Pyritic Iron
1 min.	1.67	1.97	1.91
15 min.	1.72	2.11	1.97
30 min.	1.72	2.25	1.97
60 min.	1.76	2.30	2.01

The excess of sulphur in the extract clearly indicates that even under the conditions of this experiment the organic sulphur is oxidized.

9. *Results Obtained with Dilute Nitric Acid as a Solvent.*—Samples of coal No. 7 were extracted with various dilutions of nitric acid for about 20 minutes. The first column in Table 18 gives the number of volumes to which one volume of concentrated nitric acid was diluted.

TABLE 18

EXTRACTION OF COAL NO. 7 WITH VARIOUS DILUTIONS OF NITRIC ACID

(Values given in per cent)

Dilution	Iron in Acid Extract	Sulphur in Acid Extract	Pyritic Sulphur Calculated from Iron in Acid Extract as Pyritic Iron
1	1.09	1.43	1.24
2	1.13	1.32	1.29
4	0.62	0.67	0.71
8	0.25	0.24	0.29

The last two dilutions gave very little sulphur in the extract and are probably too low. The dilution of the concentrated nitric acid to two volumes gave fairly good results, but the dilution to four volumes appeared to be the one which seemingly had no oxidizing effect on the organic sulphur. This experiment showed that concentrated nitric acid diluted to four times its volume, with sp. gr. of 1.12, possessed the maximum solvent effect on iron pyrites without attacking the organic sulphur. All subsequent extractions for pyritic sulphur were made with this strength of nitric acid.

Table 19 gives the results obtained by the use of this solvent on various hydrochloric acid extracted coals. All were treated at room temperature.

TABLE 19

EXTRACTION OF COALS WITH DILUTE NITRIC ACID

(Values given in per cent)

Sample Number	Time of Extraction	Iron in Acid Extract	Sulphur in Acid Extract	Pyritic Sulphur Calculated from Iron in Acid Extract as Pyritic Iron
7	1 hr.	1.12	1.23	1.28
7	18 hr.	1.16	1.29	1.33
7	72 hr.	1.13	1.30	1.29
7	10 days	1.20	1.36	1.37
6	4 days	1.80	2.06	2.06
6	4 days	1.80	2.06	2.06
5	4 days	0.27	0.31	0.31
5	4 days	0.27	0.31	0.31
9	4 days	0.15	0.16	0.17
9	4 days	0.15	0.16	0.17
10	4 days	0.08	0.10	0.09
10	4 days	0.08	0.10	0.09

Although several types of coal of widely varying sulphur content were treated, the amount of sulphur in each of the extracts and the amount of sulphur calculated to make FeS_2 were in every case nearly the same, as shown by the figures in the last two columns in Table 19. Dilute nitric acid is, therefore, a selective solvent for iron pyrites. The relationship between the sulphur extracted by the acid and the pyritic sulphur calculated from the iron extracted by the acid is shown graphically for coal No. 7 by the curves in Fig. 3.

The following experiment was performed to determine the best conditions for the dilute nitric acid extraction. Three samples of coal No. 7 were extracted with the dilute nitric acid; one was boiled for fifteen minutes, another was heated on the steam bath for four hours, and a third was allowed to stand at room temperature for four days. Results as shown in Table 20 were obtained.

TABLE 20

EXTRACTION OF COAL NO. 7 WITH DILUTE NITRIC ACID

(Values given in per cent)

Conditions of Extraction	Iron in Acid Extract	Sulphur in Acid Extract	Pyritic Sulphur Calculated from Iron in Acid Extract as Pyritic Iron
Boiled for 15 minutes.....	1.06	1.49	1.21
Steam bath for 4 hours.....	1.14	1.58	1.30
Room temperature for 4 days...	1.14	1.32	1.30

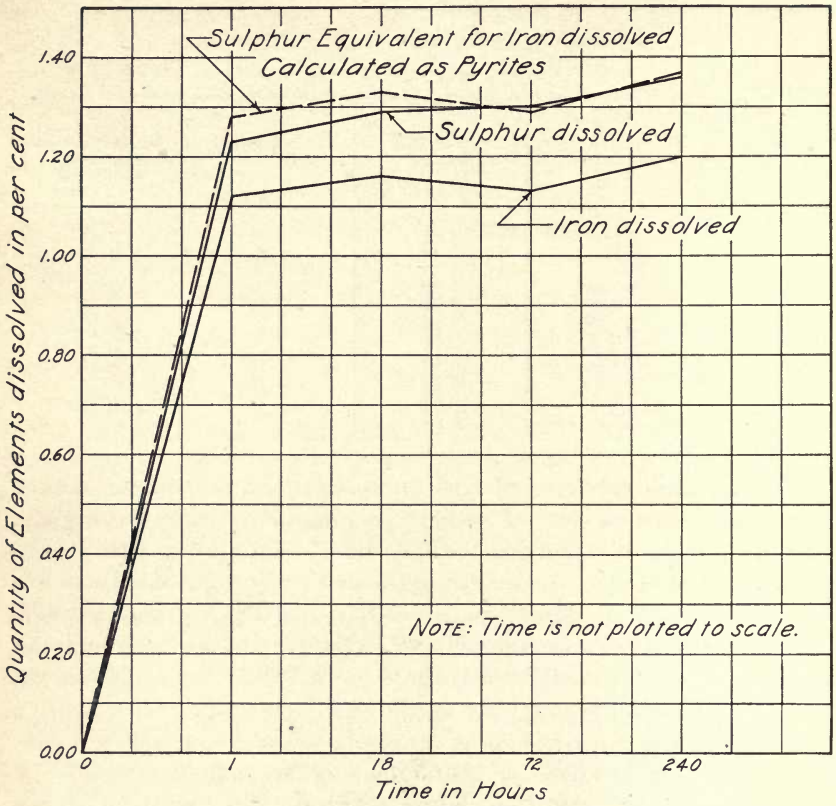

FIG. 3. CURVES SHOWING RESULTS OF THE EXTRACTION OF COAL NO. 7 WITH DILUTE NITRIC ACID

The data in Table 20 show that the quantitative extraction of the pyritic sulphur is best brought about by treatment at room temperature for several days. Any attempt to hasten the process by heat would result in the oxidation of some of the organic sulphur.

10. *The Determination and Identification of Humus Sulphur in Coal.*—The experiments on the phenol extraction of coal proved that a certain portion of sulphur existed in organic combination in the resinic type of material. The dilute hydrochloric acid extraction was the means of determining the sulphate sulphur, while dilute nitric acid quantitatively removed the pyritic sulphur from the coal. After the percentage compositions of these three known forms were added and their

sum was subtracted from the total sulphur, a quantity of sulphur was, however, shown to be still unaccounted for. Any possibility that this extra sulphur could be combined with the iron to form a sulphide higher than FeS_2 was eliminated by the nitric acid extraction experiments. It seemed necessary, therefore, to test for some other type of compound.

About five grams of coal No. 7 were extracted with concentrated nitric acid for twenty-four hours at room temperature. This treatment removed the pyritic and sulphate sulphur, but left the remainder in the residue, so that the latter could be studied conveniently by itself. Further treatment of the residue with nitric acid yielded no sulphur in the filtrate, nor did boiling with dilute nitric acid.

Guignet* and later Friswell† had observed the effect of alkalies on coal previously treated with nitric acid. Two portions of the nitric acid residue were accordingly placed in beakers, one being treated with 25 cc. of concentrated aqua ammonia and the other with a concentrated sodium peroxide solution. In both cases the thick dark brown solution described by Friswell was formed. The ammonia extract was diluted and filtered, the filtrate having a dark reddish brown color. Upon acidifying a portion of this filtrate with hydrochloric acid, a brown flocculent precipitate formed which was filtered off with the same difficulty that characterized the first filtration. The filtrate in this case was a very light yellow and contained no sulphur. This showed that the sulphur in the nitric acid residue must be present either in the ammonia insoluble substance, of which there was very little compared with the original residue, or in the flocculent brown precipitate. The qualitative analysis of this precipitate, sometimes referred to as "coal acid," showed large quantities of sulphur. An analysis of the small undissolved portion of the residue gave, furthermore, only a trace of sulphur. Anderson and Roberts‡ had found that this undissolved portion consisted of nearly 60 per cent organic matter very similar to the coal acid which would have gone into solution if it had not been occluded. This explanation could easily account for the trace of sulphur found. From this experiment, it was concluded that a knowledge of the unknown form of sulphur depended upon a study of the coal acid. The results of the sodium peroxide extraction were similar to those obtained with ammonia.

It was decided to find whether the unknown form of sulphur was

*See page 51.
†See page 51.
‡See page 52.

organic or inorganic in nature. The logical procedure was the study of the ash of the coal acid. Two grams of coal No. 7 were treated in the usual manner, the result being the formation of over 1.5 grams of ammonia soluble material. The ash content of this material was determined and when calculated on the basis of the original coal there was 0.35 per cent. The ash content of the original coal was 9.45 per cent; consequently only a very small part of the mineral matter was extracted by the ammonia. The ash was then treated with hydrofluoric and sulphuric acids to remove the silica. It was then heated to change the metals present to the oxides. This mixture of oxides was dissolved and analyzed for iron. The ash analyses by this method are:

Silica	0.10 per cent
Fe_2O_3	0.05 per cent
Other oxides	0.20 per cent
Total ash	0.35 per cent

The unknown sulphur present in the ammonia extract amounted to about one per cent. It is inconceivable that this amount of sulphur could be combined in some inorganic compound while the mineral matter was present in so small an amount. The probability is, moreover, that if such a compound existed, it would not resist the action of concentrated nitric acid and then dissolve in ammonia. The conclusion is therefore drawn that this sulphur is of an organic nature, that it exists in the humus-like portion of coal described in the literature, and that its combination in such substances is extremely stable. Because of the nature of the body in which this form of sulphur occurs, it is referred to hereinafter as humus organic sulphur in order to differentiate it from the resinic organic sulphur.

As a means of verifying the methods just given, it was decided to determine the amounts of the various forms of sulphur present in certain coals, to add these together and to see how closely the total checked with the total sulphur of the coal as determined by sodium peroxide fusion. Extremely close checks were not expected, since the combined errors of five determinations entered into each comparison. Table 21 gives the average results obtained on five different coals, all that were studied in this connection.

The agreement of the two totals in each case is very satisfactory, when the long series of manipulations which were made to obtain the sum of the four sulphur forms is considered. The last three determina-

tions gave low results, probably due to the retention of some of the humus sulphur by the residue when the ammonia extraction was performed. Such retention was particularly strong with coal No. 8, which dissolved in the ammonia with great difficulty after the nitric acid treatment. The results obtained by the various extraction methods, however, determine the general character of all the sulphur of the coal.

Effort was made to secure more specific knowledge of the organic sulphur compounds present in coal, but with negative results. Smiles's test for sulphuric acids and sulphoxides was performed by treating some finely powdered coal with concentrated sulphuric acid and then by adding a drop of anisole. The same test was applied to some of the ammonia extract, but in neither case was the positive blue color obtained. The isatin test for thiophen also gave negative results. It is therefore probable that the nature of both the resinic and humus types of organic sulphur compounds in coal is very complex.

TABLE 21

ANALYSES OF DIFFERENT FORMS OF SULPHUR IN COALS AND COMPARISON WITH TOTAL SULPHUR

(Values given in per cent)

Sample Number	4	5	6	7	8
Resinic Sulphur	0.34	0.16	0.77	0.50	0.10
Sulphate Sulphur	0.05	0.25	1.31	0.31	0.01
Pyritic Sulphur	0.85	0.31	2.06	1.36	0.29
Humus Sulphur	0.87	0.51	0.70	0.95	0.45
Total	2.11	1.23	4.84	3.12	0.85
Total S by Na_2O_2 fusion	2.14	1.20	5.00	3.31	1.02
Difference between totals	0.03	0.03	0.16	0.19	0.17

III. Changes in the Forms of Sulphur in Coal

11. *The Effect of Standing upon the Forms of Sulphur in Coal.*—A noticeable feature in the present investigation was the rapid change of certain sulphur forms to sulphate. An extreme example was given in the coal known as No. 6 which had a sulphur content of 5 per cent. After the coal stood in a tightly stoppered Erlenmeyer flask for two years, the amount of sulphate sulphur had increased from less than 0.01 per cent to 1.31 per cent. Since the percentage of soluble iron had also greatly increased, it would seem that the pyrites oxidized in some manner. The following experiments were performed to establish this as a fact.

12. *The Oxidation of Sulphur in Coal.*—Some investigation was made to determine the most favorable conditions under which coal sulphur oxidation might occur. Five grams of coal No. 1 were placed in the bottom of an Erlenmeyer flask. A tube leading nearly to the bottom of the flask was connected to a U tube filled with thoroughly moistened glass wool. A slow current of air was passed through the U tube and thence into the flask, so that the finely powdered coal was at all times exposed to fresh moist air. The flask containing the coal was kept for eighteen hours in an electric oven which was regulated to maintain a constant temperature of 60 degrees. In order to compare the effect of moist and dry air another experiment was performed in which the U tube was filled with calcium chloride instead of the moist glass wool. The results obtained are given in Table 22.

Table 22

Oxidation of Sulphur in Coal by Moist and Dry Air[1]

	Moist Air Per Cent	Dry Air Per Cent
Total sulphur in coal	2.68	
Sulphate sulphur in coal	0.045	
Sulphate sulphur in coal after oxidation by moist air	0.207	
Sulphur oxidized by moist air	0.162	
Sulphate sulphur in coal after oxidation by dry air		0.173
Sulphur oxidized by dry air		0.128

[1]It is to be noted that the moist air caused a slightly larger amount of sulphate sulphur to be formed than did the dry air.

These results showed that a comparatively small portion of the coal sulphur was oxidized under the most favorable conditions of air supply, temperature, and fineness of coal. The only condition unfavorable to a very large amount of oxidation, on the other hand, was the short time of exposure. It seemed then that the oxidation of the sulphur depended upon the time of exposure of the coal or that some factor besides simple chemical oxidation entered into the change.

The experiment just described tends to show that the oxidation of the coal sulphur was not a simple reaction in which an excess of air would cause a proportionally greater change than that which would occur in a closed flask. This condition might be explained on the basis that certain anaerobic bacteria in the coal were causing the gradual oxidation of the coal sulphur in the absence of a free access of air. An attempt was made to determine the nature of the sulphur oxidation process by means of the following experiment.

Coal No. 7 was chosen since it was a comparatively fresh coal with a low sulphate content and a high percentage of pyrites. If bacteria were the cause of the change, they would be found in the largest quantity in a coal where a very decided sulphur oxidation had occurred. Coal No. 6 fulfilled this condition; so it was chosen as the inoculating agent. Four small flasks were fitted with rubber stoppers covered with tin foil, from which were suspended glass hooks to support some wet cotton so that the interior of the flasks would be continuously moist. In two of these flasks there were placed 5 grams of coal No. 7, finely powdered, in the other two 4 grams of coal No. 7. All four flasks were thoroughly sterilized in a steam autoclave.

After sterilization, one gram of coal No. 6 was added to each of the two 4-gram flasks. There were now two flasks containing sterile coal and two others containing sterile coal mixed with a smaller quantity of old heavily oxidized coal. The set of flasks was kept at a constant temperature of 37 degrees, and the contents were analyzed later for the hydrochloric-acid-soluble sulphur and iron. In order to find the increase in the sulphur of coal No. 6, two flasks containing one gram each were used as controls for the others. Analyses of the flask contents were made nineteen days after they were placed in the incubator room and another set of analyses was made eighty-eight days later.

From these data the increase in soluble sulphur and iron in all flasks was calculated. Since the sterile flask contained five grams of coal, this increase was multiplied by four-fifths to maintain a basis of four grams. The increase in the control flask was then added. If the proc-

ess were a simple chemical reaction, the result would be equal to the increase in the sterile flask, since this one was made up of four grams of sterile coal and one gram of coal No. 6. If, however, the action of bacteria entered into the change, a larger increase of soluble sulphur and iron would be expected in the flask where the sterile and the inoculated coals were in contact than would be found by adding the increases of the two separated flasks. Table 23 gives the results obtained.

TABLE 23

RELATIVE OXIDATION OF PYRITES IN STERILE AND INOCULATED COALS

COALS	19 Days	88 Days
Increase of soluble sulphur in 4 g. sterile coal No. 7	11.88 mg.	14.00 mg.
Increase of soluble sulphur in 1 g. coal No. 6	4.40 mg.	9.40 mg.
Calculated increase of sum of two preceding items	16.28 mg.	23.40 mg.
Actual increase of soluble sulphur by analysis	16.40 mg.	34.70 mg.
Increase of soluble iron in 4 g. sterile coal No. 7	14.05 mg.	15.00 mg.
Increase of soluble iron in 1 g. coal No. 6	5.55 mg.	10.40 mg.
Calculated increase of sum of two preceding items	19.60 mg.	25.40 mg.
Actual increase of soluble iron by analysis	19.70 mg.	38.00 mg.

At the end of nineteen days there was apparently nothing unusual in the relative oxidation of sulphur in the sterile and in the inoculated coal. At the end of eighty-eight days, however, the inoculated coal showed a decidedly greater increase than did the sterile coal, the only explanation for this being some bacteriological action or perhaps catalysis. Another interesting point to be noted is that the soluble iron shows a greater increase than the soluble sulphur in every case whether the coal is sterile or not. If only pyrites were being oxidized, there would be one and one-seventh times as much sulphur as there was iron, and if other sulphur forms were oxidized the ratio would be still larger. In actual practice, however, the opposite is true. The best explanation for this discrepancy would be that some of the sulphate formed was taken up by the organic matter of the coal.

13. *Changes in the Forms of Sulphur Effected by Coking.**—When coal is subjected to destructive distillation in the absence of air, the sulphur divides between the residue and the volatile matter. The ratio between the residual sulphur and the volatile sulphur varies between rather wide limits but is fairly constant for the same coal. The factors in the coal which control this ratio have not been deter-

*See Appendix III for a historical account of similar experiments.

mined except in a general manner. Certain coal constituents, entirely separate from the sulphur containing compounds, may have an effect on the percentage of sulphur retained in the coke, but in all probability the decisive factor in determining this percentage is the relative amount of the different sulphur forms present. Since the first part of this investigation furnished a good means for determining these sulphur forms, their effect on the proportion of residual sulphur in coking was studied. The types of sulphur compounds formed in the coke were investigated. An attempt was made to determine the relation between the quantities of these types formed in the coke and the quantities of the different types of sulphur in the coal. Since the forms of sulphur in coke are entirely different from those in coal, this latter problem involved an entirely new method of procedure.

To determine the amount of residual sulphur, a one-gram sample of the coal to be tested was coked in a small nickel crucible and heated for three and one-half minutes at the full heat of the Bunsen burner and then for another three and one-half minutes with a blast lamp. A tight-fitting nickel cover prevented oxidation of the coal. The coke was carefully removed and pulverized; then it was fused with sodium peroxide in the same manner as the coal had been in another part of this investigation. After the fusion had been dissolved in water, the sulphur was determined by means of the barium sulphate precipitation. Some of the coals used in this work were the original samples, while other experiments were made with samples which had previously been extracted with dilute hydrochloric acid to remove all the sulphur in the form of sulphate. Due allowance is made in Table 24 for this removal of the sulphate form in the amount of total sulphur.

TABLE 24

FORMS OF SULPHUR IN COAL AND RESIDUAL SULPHUR REMAINING AFTER COKING

(Values given in per cent)

SAMPLE NUMBER	5a	6a	7	7a	10	10a
Total sulphur	1.08	4.00	3.31	3.00	0.95	0.93
Sulphate sulphur	0.00	0.00	0.31	0.00	0.02	0.00
Pyritic sulphur	0.31	2.06	1.30	1.30	0.10	0.10
Resinic sulphur	0.16	0.77	0.50	0.50	0.13	0.13
Humus sulphur	0.61	1.17	1.20	1.20	0.70	0.70
Residual sulphur	0.34	1.46	1.37	1.09	0.45	0.38

The coals designated by a numeral and the letter "a" are those which were extracted with dilute hydrochloric acid before coking. It

is interesting to note the difference between the amounts of residual sulphur in these coals as compared with the amounts in the corresponding coals which had not been extracted. In coal No. 7 this difference corresponds almost to the sulphur which had been removed by the dilute hydrochloric acid. In coal No. 10, however, the difference is somewhat greater than that of the sulphate sulphur. A reasonable explanation for this difference would be that coal No. 10 contained calcite, which on heating changes to calcium oxide and on uniting with some of the hydrogen sulphide would ordinarily volatilize. In the coal previously extracted with acid, however, the calcite was removed; consequently the residual sulphur was less than that in the coal extracted with acid. Cursory study of the table will show the falsity of the theory that all the organic and one-half the inorganic sulphur are volatilized during coking. In order to determine in some degree the proportion of the various sulphur forms left in the coke, the following calculations were performed. Coals Nos. 6a, 7a, and 10a were chosen since these contained less of the sulphate form to complicate the calculations and since they would be free of calcite which might enter into a secondary reaction with some of the volatile sulphur as previously explained. There would then be three unknown quantities of residual sulphur to add to the total residual sulphur which was known. Then

Let X = fraction of pyritic sulphur left in coke
Y = fraction of resinic sulphur left in coke
Z = fraction of humus sulphur left in coke

For coal No. 10a, .1X plus .13Y plus .7Z = .38
For coal No. 6a, 2.06X plus .77Y plus 1.17Z = 1.46
For coal No. 7a, 1.30X plus .5Y plus 1.20Z = 1.09

Solving these equations simultaneously, the results are as follows:

Pyritic sulphur left in coke, 16 per cent
Resinic sulphur left in coke, 95 per cent
Humus sulphur left in coke, 34 per cent

These figures doubtless would not hold for every coal since other factors enter into the retention of the sulphur in the coke. They are interesting, however, inasmuch as they show that a large amount of the organic sulphur is retained.

The retention of so much organic sulphur led to some experiments on the nature of the sulphur compounds in the coke. Although Bradbury* had believed the large portion of the coke sulphur to be organic

*See page 62.

in nature, it was difficult to conceive any organic compound withstanding the high temperature of the coking process. A more reasonable explanation would be that secondary reactions caused the organic sulphur to change into some very stable inorganic form.

A method similar to that used by Bradbury was used to determine the nature of these sulphur compounds. The finely powdered coke was placed in a small flask which was arranged so that hydrogen could bubble through a liquid in the bottom and pass out the top into an absorption tower containing a moderately strong sodium peroxide solution. The coke from one gram of the original coal was used and over this about 40 cc. of dilute hydrochloric acid (one part HCl, sp. gr. 1.19, to one part water) were poured. A slow stream of hydrogen was then conducted through the apparatus for about one hour, and finally the solution in the flask was brought to boiling to insure the removal of the hydrogen sulphide.

By this method any sulphate sulphur in the coke would go into solution and the sulphide sulphur would be carried over in the stream of hydrogen as hydrogen sulphide which would be oxidized to sodium sulphate in the sodium peroxide tower. By barium sulphate precipitation both the sulphate and sulphide forms of sulphur in the coke could accordingly be determined. The residue of this extraction was then treated with concentrated nitric acid for two hours in order to extract any pyrites which might remain. The results of this experiment on coal No. 7 and a comparison of the forms of sulphur in coke with the forms of sulphur in the original coal are given in Table 25. The percentages of sulphur and iron in the coke are estimated

TABLE 25

FORMS OF SULPHUR IN COKE COMPARED WITH ORIGINAL COAL

(Values given in per cent)

	Coal No. 7	Coke from Coal No. 7
Total sulphur	3.31	1.37
Sulphate sulphur	0.31	0.00
Sulphide sulphur	0.00	0.30
Pyritic sulphur	1.30	0.00
Resinic sulphur	0.50	0.00
Humus sulphur	1.20	0.00
Unknown sulphur	0.00	1.07
Total iron	1.87	1.87
Soluble iron	0.41	1.04
Pyritic iron	1.13	0.00
Silicate iron	0.33	0.83

on the basis of the weight of the original coal used, so that a direct comparison may be made with the coal.

The results show that the structure of the larger part of the sulphur in the coke is as yet undetermined. The concentrated nitric acid treatment removed only 0.07 per cent, so that the compounds in which sulphur is present must be very stable. The possibility of a carbon-silicon-sulphur compound presented itself, but all such compounds in the literature decompose in the presence of water or of hydrofluoric acid, releasing hydrogen sulphide. No hydrogen sulphide could be detected even when the finely powdered residue of this extraction was boiled with hydrofluoric acid. It therefore seems not to be an iron-sulphur compound, nor is it a silicon-sulphur compound. According to present data it seems to be a carbon-sulphur compound, the nature of which is as yet undetermined.

After the finely powdered coke had been boiled with dilute hydrochloric acid to release the sulphide sulphur as hydrogen sulphide, a quantity of fine aluminum turnings and some more dilute hydrochloric acid were added to the residue and the mixture again heated. Under these conditions a large amount of hydrogen sulphide was removed. This action of nascent hydrogen on the coke would also indicate the organic or carbon-sulphur character of this portion of the coke sulphur.

There are other indications of the theory that certain carbon compounds persist through the high temperature condition to which coal is subjected in the coking process. The treatment of red coke with water vapor, for example, releases a large amount of nitrogen as NH_3 which was held in some chemical combination with the carbon. In addition to ammonia, hydrogen sulphide is released from the coke by the same treatment. During the coking process, hydrogen compounds persist as high as and beyond a temperature of 1000 degrees Centigrade. These well known facts show that nitrogen, sulphur, and hydrogen may remain in organic combination at very high temperatures.

It has been previously stated that the coal material extracted by phenol consists entirely of organic matter of a resinic nature. In order to investigate the sulphur distribution during coking in this type of material, one gram of the extracted substance from coal No. 7 was coked under standard conditions. It was found that 50 per cent of this form of organic sulphur was retained in the coke; thus definite proof was obtained that a portion of the coke sulphur was organic in character and source.

Some of the indicated changes shown in Table 25 are worthy of

comment. The sulphate sulphur disappears entirely because of the reducing influence of the red hot carbon, but it does not change to the sulphide form, as will be shown later. It probably goes over to the unknown form of sulphur, since the residual sulphur is higher if the sulphate is not extracted with hydrochloric acid before coking. The source of the sulphide sulphur will be explained later. The pyritic sulphur is entirely decomposed during the coking process.

Both organic forms of sulphur in the coal change from their original form, as shown by the fact that phenol has no effect on the coke and that ammonia will not dissolve the nitric acid residue, these being characteristic properties of the two sulphur forms in the coal.

Some of the changes in the forms of iron during the coking process indicate that they are important changes. The acid soluble iron increases greatly. This change would be expected if all the pyrites decomposed. The decomposition of the pyrites also leads to a decided increase in the content of iron silicate.

The source of the sulphide sulphur in the coke was investigated. Four one-gram samples of coal No. 7 were extracted with dilute hydrochloric acid and two of these were further extracted with phenol. The residues were coked and the sulphide sulphur was determined as in the previous experiment. The original coal, as given in Table 25, yielded 0.30 per cent sulphide sulphur in the coke. After hydrochloric acid extraction of the coal, the coke still contained 0.31 per cent, and even after further extraction with phenol 0.27 per cent sulphide sulphur. These results indicate that the origin of the sulphide sulphur of the coke was not in the sulphate or resinic sulphur. In all probability the origin is in the iron pyrites.

IV. Summarized Statement of Analytical Methods

To determine the kinds of sulphur in coal, methods were developed for the quantitative analysis of each form of sulphur. The methods, for greater convenience, are brought together as follows:

(1) The sulphate sulphur is determined by extraction of the coal with dilute hydrochloric acid. For this purpose 5 grams of the coal ground to 100 mesh is extracted with 300 cc. of 3 per cent hydrochloric acid for 40 hours. The extraction is carried out in a beaker placed on a steam bath with a temperature of 60 degrees Centigrade maintained. After the extraction is filtered, the sulphate sulphur may be precipitated from the filtrate by means of barium chloride.

(2) The pyritic sulphur is determined by extraction of the coal with dilute nitric acid, after a preliminary extraction with dilute hydrochloric acid to remove the sulphate form. If the sulphate content is low, the nitric acid extraction may be performed on the original coal, allowance being made for the sulphate form by subtraction. For this purpose it is best to use one gram of the finely powdered coal covered with 80 cc. of dilute nitric acid (one part nitric acid, sp. gr. 1.42, to three parts water; sp. gr. of the mixture is 1.12). The mixture is allowed to stand at room temperature for at least four days. It is then filtered, the nitric acid driven off by evaporation to dryness and the residue taken up in some water and hydrochloric acid. In addition to determining the sulphur in this solution, the iron may also be estimated since the iron-sulphur ratio will serve as a check on the selective solution of pyrites.

(3) The resinic sulphur is determined by extraction of the coal with phenol. One-half gram of the finely powdered coal is placed in a flask fitted with an air condenser. Twenty-five cubic centimeters of phenol are poured over the coal and the extraction is carried out for 20 hours at a temperature of 140 degrees Centigrade. The best means for maintaining this temperature is a regulated electric oven. The contents of the flask are then filtered through a Gooch crucible, and rinsed with alcohol and ether. The residue in the crucible is mixed with sodium peroxide and fused. The sulphur determination on this

residue gives that portion of the sulphur not extracted by the phenol, and by subtracting this amount from the total sulphur, the resinic sulphur is determined.

(4) The humus sulphur is determined by the difference between the sum of the other three forms and the total sulphur in the coal. A direct determination may be made by extraction of the coal with ammonium hydroxide, after a preliminary treatment with concentrated nitric acid. This method is applicable only to the softer coals, the structures of which are fundamentally changed by the nitric acid treatment. For this method, one gram of the finely powdered coal is treated with 15 cc. of concentrated nitric acid for a short time (about one-half hour). This mixture is then diluted, filtered, and washed. The filter paper which contains the residue is put into 25 cc. of concentrated ammonia (sp. gr. 0.90), and allowed to stand for several hours when it is then diluted and filtered through a large fluted filter. The filtrate is evaporated to dryness and the dry residue gathered and fused with sodium peroxide. The sulphur in this fusion represents the humus sulphur.

APPENDIX I

The Constitution of Coal

The changes in the process of coal formation indicate the composition of coal, but no definite conclusions may be drawn since the chemical changes involved vary under different conditions and are obscure in all cases.

It is conceded by practically every one that coal had its origin in vast beds of vegetable matter, supplemented in most cases by animal remains. Several reasons may be advanced as proof of the vegetable origin of coal, the most important of which is the frequent occurrence of plant outlines on coal surfaces. Morphological proofs of the presence of animal residues are, however, not so plentiful, but outlines of the skeletons of fishes are often found, and they indicate the presence of water during the early stages of coal formation. Another good indication of animal remains in the coal is found by a comparison of its nitrogen content with that of pure vegetable fossils found in the same general locality. In such cases the coal contains several times as much nitrogen as the vegetable remains, this fact undoubtedly showing the presence of animal matter in the coal.*

The beds of vegetable matter have accumulated during long periods of time and complete oxidation of the organic matter is prevented by compact layers of earthy material. The chemical composition of the original plant material was similar to that of cellulose, with varying amounts of mineral matter and a large amount of water present. This vegetable sphagnum becomes peat by a process of slow decay. The chemical changes in this transformation are typical of a kind of bacterial cellulose decomposition, the products of which are the so-called humus substances, such as humic, ulmic, crenic, and apocrenic acids. None of these products is a definite chemical compound since each product represents merely a type of substance. As peat is acidic in character, nearly all of it will dissolve in an alkaline solution. Underground waters carry lime and iron salts in solution to the peat and cause the formation of insoluble calcium and iron salts of the acids. Although calcium and iron are found in the ash of peat, the calcium rarely exists as the carbonate, as might be expected.† The change from vegetable

*Clarke, F. W., "The Data of Geochemistry," p. 654, 1908.

†Berichte der Deutschen Chemischen Gesellschaft, Vol. 15, p. 2961, 1882.

matter to peat is accompanied by loss of both water and oxygen, so that the net result is a gain in the carbon content and a loss of both hydrogen and oxygen. Each step in the process of change from peat to anthracite coal involves, moreover, the same result—a continuous increase in the percentage of carbon, a decrease in the percentage of hydrogen and a decrease of oxygen until nearly all the oxygen has disappeared.

Lignites form the connecting link between the distinctly vegetable peat and the rock-like bituminous coal. These are soft deposits and generally light brown. They contain organic sulphur as well as pyrites or marcasite and sulphates such as gypsum.*

The changes from lignites to bituminous coal and then to anthracite coal give no suggestion of the chemical composition of coal, except perhaps its tendency to approach a hydrocarbon. The earlier chemical changes are, according to White,† largely bio-chemical, while the later changes are more distinctly dynamo-chemical.

Nearly all the foregoing discussion refers to the carbon, hydrogen, and oxygen in the coal. The methods of formation of the nitrogen and sulphur compounds depend upon the combination of these elements in the coal. A large part of the nitrogen of the coal comes from the remains of animals, and since the remainder comes from the plant substance, it must exist as organic amino nitrogen, unless there have been nitrifying bacteria present which cause oxidation.

The sulphur of the coal may come from two entirely different sources. The original plant and animal substances from which the coal was formed undoubtedly contained organic sulphur. Whether this organic sulphur changes during the coal making process is not known, but there is evidence that it may furnish the sulphur for the pyrites and marcasite of the coal. Since iron and calcium are precipitated from ground waters by the humus acids of the peat as it undergoes change, hydrogen sulphide waters percolating through the coal substance would change the iron to the sulphide and thence to pyrites or marcasite. If sulphur is found in the form of sulphate in fresh coal, it is found only in small percentages.

Where aerated water has the chance to come in contact with pyrites, however, a very slow oxidation occurs. Winchell‡ states that he made tests with aerated water acting on pyrites. At the end of one month,

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*Dana, James D., "The System of Mineralogy," 6th ed., p. 1010, 1895.
†Economic Geology, Vol. 3, p. 293, 1908.
‡Economic Geology, Vol. 2, p. 290, 1907.

he found that neither iron nor sulphur had gone into solution. At the end of ten months, 0.2 g. of pyrites had been oxidized and there were in the solution 27.7 mg. of ferric sulphate and 5.7 mg. of sulphuric acid per liter with traces of ferrous salts and sulphur dioxide. These tests show that it is possible for comparatively large quantities of sulphate to be formed in the coal, provided the flow of the aerated water does not leach out the compounds so fast as they are formed. Any sulphate formed would have the tendency to change to calcium sulphate or another sulphate not so soluble as the ferric salt.

It has also been found, according to Stokes,* that alkaline waters decompose pyrites and marcasite to ferric oxide. The sulphur decomposes in the form of alkali sulphides and thio-sulphates. It is stated that oxygen is not necessary for this action to occur. These examples suggest that pyrites may undergo secondary changes while in the underground coal.

There is a third source possible for the sulphur in coal besides the original vegetable matter and percolating waters. While the coal is still in the process of formation, it is very likely to be mixed mechanically with detritus, which may account for not only a large part of the ash of coal but also for some of the inorganic sulphur.†

A general method used to determine the constitution of coal is that of destructive distillation. This method has been studied more thoroughly than the others because of the commercial importance of coking processes and gas manufacture; yet it is the poorest from the standpoint of determining the real nature of the coal substance. It is now a well proved fact that all the products of distillation of coal do not come from the coal by simple distillation, but that every one of them is the result of the decomposition of more complex compounds. A discussion of the destructive distillation must be limited to only those facts which tend to show the nature of the coal substance.

The products resulting from the destructive distillation of coal consist of gaseous, liquid, and solid condensate and a residue which is largely carbon mixed with the ash of the coal. Among the volatile products are ammonia, carbon dioxide, hydrogen sulphide, hydrogen, methane, carbon monoxide, nitrogen, acetylene, ethylene, other hydrocarbons, pyridin, phenol, benzene, toluene, xylene, naphthalene, anthracene, phenanthrene, cresol, and a great variety of other aromatic compounds. Because of the predominant presence of ring hydro-

*Economic Geology, Vol. 2, p. 14, 1907.

†Hinrichsen, F. W., and Taczak, S., "Die Chemie der Kohle," p. 124, 1916.

carbons and their derivatives, it has been supposed that the original coal consisted of ring-like compounds.

R. Meyer* has an interesting theory concerning coal structure. He believes the main part of the coal to be composed of compounds which are merely polymers of acetylene and which change very readily into acetylene on heating. The nitrogen exists in such a form that it will come out as ammonia or hydrocyanic acid. When the coal is being distilled, these primary decomposition products unite in various combinations to give the ordinary distillation products. Meyer performed some experiments to substantiate this theory. By passing acetylene, mixed sometimes with ammonia or hydrocyanic acid, through a heated tube, he obtained a variety of products, among which were benzene, toluene, diphenyl, styrol, inden, napthalene, anthracene, phenanthrene, pyrene, fluorene, acenaphten, chrysene, hexylene, pyridin, anilin, carbazol, and benzonitrile. All these products, with the exception of the hexylene, have been separated from coal tar. His theory of coal composition is undoubtedly at least partially correct, but whether it applies to all the organic compounds of the coal is doubtful from such evidence.

The largest part of the sulphur of coal comes off on distillation as hydrogen sulphide, but there are also thiophen compounds in the tarry distillate. The presence of hydrogen sulphide indicates not only the sulphur lost by the pyrites on heating, but may show the presence in the coal of complex organic sulphur compounds of a protein nature. From Meyer's theory the thiophen ring compounds could be formed by a secondary reaction between acetylene and hydrogen sulphide; therefore the presence of thiophen or its derivatives could hardly be considered as proof of the existence in the coal of cyclic organic sulphur compounds.

Another method for determining the composition of coal is by means of selective solvents. This is by far the best of the three methods. Any constituent obtained will be in the condition in which it existed in the coal or because of the simplicity of the extraction the original substance may be easily deduced. This method of analyzing the coal structure is increasing in use.†

The solubility of the humus acids of peat in alkalies has been previously mentioned. F. G. Kaufmann‡ has regarded peat as a mixture of

*Berichte der Deutschen Chemischen Gesellschaft, Vol. 45, p. 1609; Vol. 46, p. 3183, 1913.
†Journal of the Society of Chemical Industry, Vol. 36, p. 176, 1917.
‡Verhandlungen der Kaiserlich-Königlichen Geologischen Reichsanstalt, Vol. 15, p. 283, 1885.

two substances, dopplerite, the portion soluble in caustic alkali solutions* and another substance consisting of partly decomposed vegetable matter.

By the solvent method, peat has also been found to contain resinous substances as high as 3.26 per cent of the content of the peat. The resins are extracted by using hot ether or alcohol as solvents.†

Resinoids and fossil hydrocarbons are abundant in lignites. The fossil hydrocarbons are generally visible as definite masses. The resinoids are very often disseminated throughout the coal; consequently solvents must be used as extraction agents. Benzene and other organic solvents will extract the resins, which have been found to be indefinite in composition. Watson Smith‡ states that he obtained 9.5 per cent of extractive matter by the action of benzene on a Japanese lignite.

Humus compounds are present in lignites, but not to so great an extent as in peat; hence xyloid lignite is found to dissolve in caustic alkali to an extent somewhat less than peat, and very little solvent action can be obtained with the more compact lignites.¶ Bituminous and anthracite coals are not dissolved at all by alkaline solutions; so there must be a gradual destruction of the humus compounds during the coal evolution process. At times humus bodies are found in large percentages. Among the "paper coals" of Russia are found deposits of humic matter soluble in ammonia.§ In Bohemian brown coal von John found a humus acid, with the approximate formula $C_{46}H_{46}O_{25}$, soluble in ammonia or sodium carbonate.** A fossil humus from a Tertiary deposit near Cassel, Germany, furnishes the pigment known as Cassel brown.

Fremy†† states that lignites are soluble in alkaline hypochlorites, while the older coals are not. Nitric acid attacks lignites very vigorously, and causes the formation of a yellow resinous body which will dissolve in an excess of the nitric acid or in an alkaline solution. This property of the lignites is very important from the standpoint of coal

*Dana, James D., "The System of Mineralogy," 6th ed., p. 1014, 1895; Claessen, C., "Ueber Dopplerit," Chemiker-Zeitung, Vol. 22, p. 523, 1898; Alexejew, W., "Ueber Elaterit und Dopplerit," Zeitschrift für Krystallographie und Mineralogie, Vol. 20, p. 187, 1892.

†Jacobsen, Oscar, Annalen der Chemie und Pharmacie, Vol. 157, p. 240, 1871; Mulder, idem, Vol. 32, p. 305, 1839.

‡Journal of the Society of Chemical Industry, Vol. 10, p. 975, 1891.

¶Fremy, Comptes Rendus de l'Académie des Sciences, Vol. 52, p. 114, 1861.

§Zeiller, M. R., "Note sur la compression de quelques combustibles fossiles," Bulletin de la Société Geólogique de France, Vol. 12, series 3, p. 680, 1884.

**Verhandlungen der Kaiserlich-Königlichen Geologischen Reichsanstalt, p. 64, 1891.

††Comptes Rendus de l'Académie des Sciences, Vol. 52, p. 114, 1861.

constitution and has been used with marked success in the present research to determine several unknowns. This treatment of coal with nitric acid cannot be regarded as a simple solution method; yet it is included with this method because of the close analogy existing between the two.

E. Guignet* was the first investigator to study in much detail the action of nitric acid upon coal, and he concluded that the products formed were similar to the nitrocelluloses. This work was followed by that of R. J. Friswell,† who fails to acknowledge the previous work of Guignet on this subject but describes the phenomenon accurately, as follows:

"If bituminous coal in fine powder be covered with rather more than double its weight of 49 per cent nitric acid, the mass rapidly becomes warm, and dense red fumes are given off. If 90 g. of coal and 200 cc. of the acid are taken, the action is extremely brisk, and the frothing so violent that a 2000 cc. flask is requisite to contain the mass. In about 30 minutes the action slackens, and heat being now applied, the action is kept going at such a rate that a brisk evolution of gas continues; the solution is gradually raised to the boiling point and there maintained, the total time occupied being about 6 hours. The whole is now diluted, poured into a filter, and well washed. The filtrate consists of dilute nitric acid, with salts of calcium, iron, etc., in solution. The black residue on the filter is apparently unchanged coal. When washed free from acid, the residue is introduced into a flask and boiled with a dilute solution of sodium carbonate: nearly the whole dissolves, carbonic anhydrids being briskly evolved. The resulting deep black-brown colored liquid filters with great difficulty, but by careful treatment with water in deep vessels the insoluble matter from the 90 g. of coal was found to be 12.5 g., consisting of coarse particles of coal, sand, etc."

He proceeds to say that with some coals practically all the organic matter of the coal could be taken into solution by nitric acid, particularly if the coal were very finely divided. If the filtered solution is acidified with hydrochloric acid, a "bulky, deep brown-black, flocculent precipitate" is formed, which is insoluble in water containing traces of mineral salts or acids but which is fairly soluble in boiling distilled water from which it separates again on cooling.

This "coal acid," as it is sometimes called, when dried at 100 degrees Centigrade forms shining black masses with conchoidal fracture. When

*Idem, Vol. 88, p. 590, 1879.

†Proceedings of the Chemical Society, Vol. 8, p. 9, 1892.

heated on platinum foil, the substance swells into a brilliant black mass, resembling very much in this respect a nitro compound of high carbon ratio. To investigate this resemblance, Friswell attempted reduction by means of zinc dust and caustic soda and also by sodium amalgam and acid reducing mixtures, but in no case was there formed a nitro reduction product. Dry distillation with zinc dust drove off the nitrogen in the form of ammonia, pyridin, and cyanides.

The coal acid seemed to be similar to the humus acids of peat, but it is different in several respects. In the first place the coal acid is not hygroscopic as humus acids have been found to be. After the coal acid is dried, it may again be dissolved, but the humic acid will not dissolve. The coal acid, furthermore, does not yield acetic acid on dry distillation. Some of the humus acids yield ammonia when boiled with alkalies, differing in this respect from coal acid as might be expected from evidence that it is a nitro compound.

This work was followed by that of Anderson and Roberts,* who investigated particularly the ultimate composition of the coal acid and its relationship to the type of coal. They found that the substance consisted of carbon, hydrogen, oxygen, nitrogen, and sulphur together with a small quantity of ash, mostly iron oxide. For the same type of coal they found the composition almost constant. After the coal was treated with nitric acid and then with ammonia, only a very slight residue remained. This residue was found to consist of 36 per cent mineral matter and occluded organic matter which was very similar to the coal acid and which would probably have gone into solution had it not been so intimately mixed with the other residual substances. They assert that the presence of sulphur in the coal acid is the first proof of the existence of organic sulphur in the coal.

In order to get some more data on the nature of the coal acid, Anderson and Roberts heated samples of Ell coal for four hours in a stream of carbon dioxide at 300–315 degrees Centigrade. At the end of this time the dry Ell coal was found to have lost about 9.5 per cent of its weight. The residue was treated in the usual manner to obtain the coal acid, and an ultimate analysis was then made. After the analysis of this substance was compared with that of the coal acid from the original coal, the two were found to be practically identical in ultimate composition; consequently the conclusion is drawn that the "nitrogenous molecule" of the coal is stable at that temperature. Other experiments and particularly portions of the present research show that this organic

*Journal of the Society of Chemical Industry, Vol. 17, p. 1013, 1898.

component, comprising the larger part of the coal matter, is unusually stable, not only to heat, but to many strong chemical reagents.

More work was done on coal solvents by a committee of the British Association,* but this work was incomplete. In addition to other solvents, the action of a mixture of hydrochloric acid and potassium chlorate was tried on coals. This oxidizing reagent seemed to differ in its mode of action from nitric acid in that the final product appeared to be a chlorinated substance.

Considerable investigation has been undertaken by E. Donath on the reaction of nitric acid with coal.† He finds that dilute nitric acid will react vigorously with lignite, but has no action on bituminous coal. He concludes, therefore, that the one is not a transformation product of the other, but that they have entirely different origins. This conclusion, although partially true, is probably too sweeping in character.‡

Franz Fisher in recent years has tested the action of ozone on coal.¶ He finds that after ozone has been allowed to act on finely powdered coal, the coal is in such a condition that as much as 92 per cent of it may be soluble in water. The substance appears to be acidic in character, and is probably intimately related to the product resulting from the action of nitric acid on coal.

The solution methods so far given have been particularly of a destructive nature to the coal substance. Other investigations have been made with simple solvents, which have presumably extracted the unchanged coal constituents. The first reference to work of this kind is in a report to the Commissioners of the 1851 Exhibition by Doctor Smythe of Göttingen. He tried the following solvents, given in the order of their extractive ability, on a brown Cologne coal, benzene, chloroform, alcohol, ethyl ether, petroleum ether, and acetone.§

Reinsch** in 1885 tried the action of alkaline solutions on the raw coals. He believed coals to be composed of two characteristic substances, which could be distinguished by this reaction.

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*Annual Report, British Association, 1894, p. 246; 1896, p. 340.

†Chemiker-Zeitung, Vol. 29, p. 1027, 1905; Zeitschrift für anorganische Chemie, 1906, p. 557; Oesterreichische Zeitschrift für Berg-und Hüttenwesen, Vol. 51, p. 310, 1903; Chemiker-Zeitung, Vol. 28, pp. 180, 953, 1904.

‡Clarke, F. W., "The Data of Geochemistry," p. 653, 1908.

¶Berichte der Deutschen Chemischen Gesellschaft, Vol. 49, p. 1472, 1916; Engineering, Vol. 103, p. 296, 1917.

§Bedson, P. Phillips, "Notes on the Proximate Constituents of Coal," Journal of the Society of Chemical Industry, Vol. 27, p. 149, 1908.

**Dingler's Polytechnisches Journal, Vol. 256, p. 224, 1885; Journal of the Chemical Society, Abstracts, Vol. 48, p. 876, 1885.

In 1901 Baker investigated the action of pyridin on coals.* He found that only a very small percentage of the anthracite coal was soluble, while in some cases as much as 20.4 per cent of bituminous coals went into solution. The solutions were brown colored and sometimes fluorescent. No relationship could be obtained in the proportion of the elements in the coal, the residue, and the extract. Anderson and Henderson also did some work on the pyridin solution of coal.† This investigation was undertaken with three types of coal, Japan, Bengal, and Scotch, and the extracts from all seemed to be similar in properties and chemical constitution.

A similar research was carried out by Donath on a German coal.‡ By treating a coal with pyridin, he obtained a brownish-red solution, which gave a flocculent brown precipitate on addition of water or petroleum ether.

Bedson in 1908 performed a number of experiments with the pyridin extraction of coal.¶ He found that gas coals yielding from 64 to 66 per cent of coke gave from 24 to 35 per cent of pyridin soluble material. Bedson thought that the pyridin soluble substances had some relationship to the volatile matter, but this supposition seemed to be disputed by the work of Dennstedt, Hassler, and Bünz,§ who found that coals yielding from 62 to 87 per cent of coke (on an ash free basis) gave a pyridin extract which had only from 0.6 to 18 per cent of soluble matter. Wornast tried out the relationships on different gas coals.** A Lothringer gas coal yielding 50 per cent coke gave an extract of 12 per cent, while a Westphalian gas coal yielding 62 per cent coke gave 29 per cent. Rau concludes from results of this sort that in general more recent coals give a smaller extract than gas coals, that the maximum extract is reached at a coke yield of about 65 per cent, and that the amount of extract again decreases until anthracite coals give almost nothing.

Lewes investigated the action of pyridin on coal, particularly with reference to its effect on the coking properties.†† He states that the coking power of a coal is mostly or entirely removed by the pyridin

*Transactions, North of England Institute of Mining and Mechanical Engineers, Vol. 50, (2), p. 23, 1901: Journal of the Society of Chemical Industry, Vol. 20, p. 789, 1901.

†Journal of the Society of Chemical Industry, Vol. 21, p. 242, 1902.

‡Zeitschrift für angewandte Chemie, Vol. 19, p. 657, 1906.

¶Journal of the Society of Chemical Industry, Vol. 27, p. 147, 1908; Journal für Gasbeleuchtung, Vol. 51, p. 627, 1908.

§Zeitschrift für angewandte Chemie, Vol. 21, p. 1825, 1908.

**Rau, O., "Ueber die Fortschritte in der Gewinnung der Nebenprodukte beim Kokereibetriebe," Stahl und Eisen, Vol. 30, p. 1236, 1910.

††Progressive Age, Vol. 29, p. 1030, 1911.

extraction, and ascribes this fact to the removal of resinic bodies necessary to the coking of a coal. He explains the retention of the coking properties by some coals even after pyridin extraction by assuming the presence of a resinic body not soluble in the pyridin. Lewes, in addition to previous investigators, had noticed that some coals yielded a higher percentage of volatile matter after rather than before extraction, and he believed that this phenomenon was due to the retention of some of the pyridin. His conclusions on the nature of the resinic bodies were that they were of two kinds, "the one easily oxidizable, soluble in pyridin and saponifiable by alkalies, and which on weathering is oxidized into a humus body with the evolution of water and carbon dioxide, and is responsible for the heating of coal in storage; the other class non-oxidizable, not saponified by alkalies, and forming with pyridin a compound insoluble in excess of the reagent, and this class may be the hydrocarbons from decomposed resins, as the residue in which they are present yields rich liquid hydrocarbons, as tar and pitch, but not rich in gas."

Wahl in 1912 investigated the action of certain coals toward pyridin.* He found the volatile matter in the coal higher than that of the residue after pyridin extraction. The coke produced from the residue was more compact than that of the original coal.

In 1912, Frazer and Hoffman published the results of their researches on the action of phenol on coal.† Before deciding on the use of phenol as an extractive agent, they tried various other solvents, but they found that phenol, pyridin, and anilin gave the best results. A non-coking bituminous coal from Franklin County, Illinois, was selected for the investigation. A large quantity was finely ground and extracted with phenol at 140 degrees Centigrade for about 10 hours, and then the mixture was filtered. The extract was a dark red and was concentrated under diminished pressure to separate most of the phenol; then the remainder of the phenol was washed out by means of sodium hydroxide. The residue from the phenol extraction was not studied any further, but the phenol soluble material was treated with a 10 per cent sodium hydroxide solution. Both the soluble portions of this sodium hydroxide treatment were extracted with ether. In both cases, the ether insoluble compounds showed not only carbon, hydrogen, and oxygen, but also sulphur and nitrogen, while the ether soluble compounds showed only the first three. Each of the four mixtures was further separated by

*Comptes Rendus de l'Académie des Sciences, Vol. 154, p. 1094, 1912.

†"The Constituents of Coal Soluble in Phenol." U. S. Bureau of Mines, Technical Paper 5, 1912

means of other solvents and fractional distillation in certain cases, until about thirty different substances had been obtained and analyzed. Frazer and Hoffman assumed these substances to be the same as in the coal, and thought the evidence was fairly conclusive that these substances nearly approached being pure compounds.

In 1913, Pictet and Ramseyer extracted coal with benzene. The oil so obtained was fractionated by distillation and the different fractions studied. From this investigation, they believe coal to contain polymerized hydroaromatic hydrocarbons.*

From their work on the phenol extraction of coal in 1913, Clark and Wheeler believed coal to be composed of two types of substances.† They called them the "hydrogen yielding" and the paraffin yielding, respectively. The distinction refers principally to the ease of decomposition, since it has been found that there is a large amount of hydrogen released between 750 and 800 degrees. They considered the pyridin insoluble substance to be a degradation product of cellulose. They were somewhat doubtful whether the pyridin extract consisted entirely of resinous material, but when the pyridin soluble substance was extracted with chloroform, nearly pure resinous material was dissolved. This work of Clark and Wheeler as well as that of White‡ and Jeffrey¶ has fairly definitely established the hypothesis of the two general types of bodies in coal, first the degradation products of cellulose, and secondly the resinic type of bodies.

In conformity with this idea, Parr and Hadley studied the phenol extraction of coal, with particular reference to the properties of both the extract and the insoluble residue.§ The temperature in all these experiments was above 110 degrees Centigrade. The results of this work may briefly be summarized as follows. The amount of soluble material varied in different types of coal, for example, Vermilion County coals yielded from 35 to 40 per cent of soluble matter, Madison and Montgomery county coals from 30 to 35 per cent, and Williamson County coals only from 20 to 30 per cent. All these figures are on an ash and moisture free basis. The residue from the extraction would not coke; thus the coking constituent was shown to be in the phenol extract. Both residue and extracted material oxidized at room tem-

*Archives des Sciences Physiques et Naturelles, Vol. 34, series 4, p. 234, 1912; Chemical Abstracts, Vol. 7, p. 1496, 1913.

†Transactions, Journal of the Chemical Society, Vol. 103, p. 1704, 1913.

‡U. S. Geological Survey, Professional Paper 85-E, 1914.

¶Proceedings of the American Academy of Arts and Sciences, Vol. 46, p. 273, 1910.

§"The Analysis of Coal with Phenol as a Solvent." Univ. of Ill. Eng. Exp. Sta., Bul. 76, 1914.

perature and more rapidly at 100 degrees Centigrade. The extract contained more volatile matter than did the residue, although the ultimate composition was about the same in both cases, and the gases released have about the same composition. Some other facts concerning the oxidation of coal were established by this process.

The method of extraction which Parr and Hadley used was continuous in its action, that is, fresh solvent was at all times acting on the finely powdered coal. The coal was contained in an extraction thimble supported in a Kjeldahl flask, in the bottom of which was the boiling phenol. The vaporized phenol was condensed at the top of the flask by a boiling toluene condenser, so that the phenol would drop on the coal at a temperature of 110 degrees Centigrade or more. Carbon dioxide was passed through the extraction flask to prevent oxidation by the air.

Regarding the distribution of sulphur between the residue and extract, the following statement is made:

"It is to be noted that the percentage of sulphur in the residue is high. This is to be accounted for by the fact that the residue contained practically all of the ash that was present in the coal. That there was some sulphur in the extract was taken to indicate that a part of the sulphur in the coal was present in the organic form."*

*Parr, S. W., and Hadley, H. F., "The Analysis of Coal with Phenol as a Solvent." Univ. of Ill. Eng. Exp. Sta., Bul. 76, p. 27, 1914.

APPENDIX II

The Development of a Method for Analyzing the Different Forms of Sulphur in Coal by Other Investigators

Many methods have been devised for the determination of the total sulphur in coal, all of them depending on the use of an oxidizing reaction sufficiently strong to convert every form of sulphur in the coal into soluble sulphate. The practical importance of total sulphur determinations has long been recognized, because in the combustion of high sulphur coals large quantities of corrosive gases are released and because in coking processes a large percentage of the sulphur is retained in the coke.

Any relationship, however, between the amount of total sulphur and the amount of sulphur in flue gases or coke has never been found, because the sulphur does not exist in only one form, but in several entirely different combinations. Any method for analyzing the separate forms of sulphur in coal would help to solve these problems. Engineers are now realizing the importance of such a method, since data obtained from such analyses would give information necessary in deriving the correct heating value of the coal, the amount and character of corrosive gases, and the distribution of sulphur in coking, while a total sulphur analysis gives these data in only a very general manner.* Some method for obtaining these data would be of scientific value, since it would be one more step toward the determination of coal constitution.

W. A. Bradbury in 1878 indicated that sulphur exists in coal in organic combination.† The first method proposed to determine this organic sulphur separately from the inorganic was that of T. M. Drown.‡ He treated the finely powdered coal with a sodium hydroxide solution of 1.25 sp. gr., which had previously been saturated with bromine. After this sodium hypobromite treatment, the solution was acidified with hydrochloric acid, and then, if necessary, the hypobromite treatment repeated on the residue. The solution was evaporated to get rid of silica, taken up in hydrochloric acid and water, and the sulphate precipitated. Drown claims that only the sulphur existing as pyrites

*Martineau, Albert, "The Effect of Sulphur on the Value of Coal," Electrical World, Vol. 69 p. 698, 1917.

†Chemical News, Vol. 38, p. 147, 1878.

‡Ibid, Vol. 43, p. 89, 1881.

and sulphate are taken into solution by this method; therefore the organic sulphur is left in the residue.

The same investigator also tried the effect of hydrochloric acid and potassium chlorate on the same coals. By this method, the coals having a small percentage of pyrites gave the same results as with the other method, but those containing much pyrites gave higher results. With the hypobromite method very good checks were obtained, but Drown could offer no proof that only the inorganic sulphur was dissolved.

The next year Helm attacked the problem from the side of the organic sulphur constituents.* He tried the action of alcohol, ether, benzene, and alcoholic potassium hydroxide on coal with the idea of extracting all the organic sulphur. Nothing definite, however, resulted from this work.

Ferdinand Fisher followed up the work of Drown on the separation of the inorganic from the organic sulphur.† He treated samples of powdered coal with water and then added bromine gradually. At the end of five hours the reaction was complete, but when the water had been heated to 70 degrees Centigrade before beginning the experiment, the time required was only one-half hour. The mixture was filtered, and sulphur and iron were determined in the filtrate.

Bromine reacts with pyrites as follows:

$2\ FeS_2$ plus $15\ Br_2$ plus $16\ H_2O = Fe_2(SO_4)_3$ plus H_2SO_4 plus $30\ HBr$

The pyrites should therefore all pass into solution, and both the iron and sulphur would be found in the filtrate. Fisher at this time recognized that iron existed in other forms besides pyrites, since the residue from these extractions contained considerable iron. The ratios between the percentages of iron and sulphur in the filtrate were variable and did not indicate that only the pyrites was extracted. In some cases the sulphur was higher than indicated by the formula FeS_2, while in others the sulphur was lower. This latter discrepancy was explained by assuming that another form of iron went into solution or that all the sulphur had not been made soluble. Apparently no dilute hydrochloric-acid-soluble-iron nor sulphur had been determined on the coals used as samples.

Fisher believed that his method was not safe as a means for determining the inorganic as distinguished from the organic sulphur, since some of the organic sulphur might be oxidized by the bromine to sulphate and since some of the sulphate might be taken up by unsaturated

*Archiv für Pharmacie, 38, 1882.

†Zeitschrift für angewandte Chemie, p. 764, 1899.

organic compounds. From his investigations, he came to the conclusion that the larger part of sulphur in coal was in the organic form, a fact which had not received much consideration before that time.

In more recent years a method has been used for the determination of the different forms of sulphur in coal depending on certain assumptions regarding the structure of coal. In the first place, all the iron not soluble in dilute hydrochloric acid is assumed to be combined as pyrites, and the pyrite sulphur is therefore estimated on the basis of FeS_2. Iron, however, may exist as the silicate, sometimes in large quantities; so there is a very weak point in this scheme of analysis. The sulphur soluble in dilute hydrochloric acid is taken as the sulphate sulphur, undoubtedly a correct assumption. After these two forms of sulphur are determined, the others are regarded as organic sulphur. No proof has as yet been given, however, that the remainder is entirely organic sulphur. Because of the assumptions on which this method depends and the indirect manner of obtaining results, some effort has been made to get a more direct and more nearly exact procedure.

In 1915, E. F. Charlton performed some experiments in the Chemistry Laboratory of the University of Illinois to obtain a direct method for the determination of organic sulphur in coal. His process was essentially the phenol extraction method of Parr and Hadley, previously described. The residue and extract were therefore analyzed by sodium peroxide fusion for their sulphur content. His procedure was based on the theory that the residue or insoluble portion of the coal left after the phenol treatment contained all the inorganic sulphur and that the portion soluble in phenol contained all the organic sulphur. This hypothesis seemed to apply in the case of low-sulphur coals, but in high sulphur coals the amount of sulphur remaining in the insoluble residue was so excessive as compared with iron present that it was impossible to assign such sulphur to any mineral combination. Hence the question arose whether the phenol was taking out all the organic sulphur and leaving an unknown inorganic form still remaining in the residue, or whether the phenol was indeed not extracting all the organic sulphur. That the extracted sulphur compounds were organic was definitely proved by the fact that the soluble material left no ash on ignition.

APPENDIX III

Changes in the Forms of Sulphur in Coal

When coal is allowed to remain exposed to the air for any length of time, certain fundamental changes take place, the exact nature of which has been only partially determined. Since these changes affect the heating and coking value of the coal to a great extent, numerous investigations have been made in order to learn the conditions which will prevent the occurrence of these changes.

Parr and Hamilton* have reviewed some of the work done on this problem and from their own observations have come to the following conclusions:

(1) Submerged coal loses no heat value.
(2) Outdoor exposure causes loss of heat value from 2 to 10 per cent.
(3) High sulphur coals oxidize in the open more than under cover, since the oxidation of the sulphur promotes other disintegration.
(4) The main loss occurs in the first five months after mining.

Even when coal samples were sealed tightly to eliminate all air, considerable deterioration occurred. Parr and Wheeler† have shown that the heating value of coal kept under these conditions may decrease as much as 4.3 per cent. Gases seem to be given off continually, but with the greatest volume during the first two or three weeks of storage. Oxidation also occurs, due probably to the absorption of some oxygen.

In 1910 M'Callum conducted an investigation to determine the effect of different percentages of organic and inorganic sulphur in the coal on the amount of residual sulphur when the coal was coked.‡ The coal used was from Nova Scotia. It was finely ground and then separated into different samples by using solutions of different specific gravities. By this method, five samples were obtained and analyzed for their organic and inorganic sulphur content. This analysis was made by calculating the sulphur which would unite with the total iron to form pyrites and by calling this the inorganic sulphur. The remaining sulphur was considered as organic. M'Callum claimed that no sulphate

*Economic Geology, Vol. 2, p. 693, 1906.
†"The Deterioration of Coal Samples." Univ. of Ill. Eng. Exp. Sta., Bul. 17, 1907.
‡Chemical Engineer, Vol. 11, p. 27, 1910.

sulphur was present. He believed also that silicate iron was so low that it might be disregarded. He apparently did not determine the dilute-hydrochloric-acid-soluble iron. With these very evident sources of error in his scheme of analysis, however, he found that the five samples varied in organic sulphur content from 37 per cent of the total sulphur to 85 per cent.

Each of these samples was then coked to get the relative amounts of volatile and residual sulphur. Where the organic sulphur was present as 37 per cent of the total sulphur, the volatile sulphur ran 33 per cent, and where the organic sulphur was 85 per cent, the volatile sulphur ran 52 per cent. No definite relationship seemed to exist between the amount of organic sulphur and the volatile sulphur, except that, in general, where the organic sulphur was high, the volatile sulphur was also high. This experiment seemed to disprove one of the old theories that coking a coal drove out all the organic sulphur and one-half of the pyritic sulphur. His conclusion was that "a very considerable part of the organic sulphur is volatilized."

Bradbury* as early as 1878 studied the forms of sulphur in coke. He treated the finely powdered coke with dilute hydrochloric acid and collected and determined all the hydrogen sulphide given off. The dilute hydrochloric acid solution was analyzed for sulphate sulphur and for iron. The residue was then treated with concentrated aqua regia and potassium chlorate and this solution was also analyzed for sulphur.

His results showed that only a small portion of the total sulphur of the coke existed as sulphide sulphur, that practically none existed as sulphate sulphur, and that even the strong oxidizing influence of the aqua regia-potassium chlorate mixture failed to take out more than a small part of the total sulphur. From these results he concluded that the larger part of coke sulphur was in an organic form. Practically all the iron of the coke was dissolved by the dilute hydrochloric acid; thus the iron pyrites of the original coal had been completely decomposed during the coking process.

*Chemical News, Vol. 38, p. 147, 1878.

LIST OF
PUBLICATIONS OF THE ENGINEERING EXPERIMENT STATION

Bulletin No. 1. Tests of Reinforced Concrete Beams, by Arthur N. Talbot. 1904. *None available.*

Circular No. 1. High-Speed Tool Steels, by L. P. Breckenridge. 1905. *None available.*

Bulletin No. 2. Tests of High-Speed Tool Steels on Cast Iron, by L. P. Breckenridge and Henry B. Dirks. 1905. *None available.*

Circular No. 2. Drainage of Earth Roads, by Ira O. Baker. 1906. *None available.*

Circular No. 3. Fuel Tests with Illinois Coal (Compiled from tests made by the Technological Branch of the U. S. G. S., at the St. Louis, Mo., Fuel Testing Plant, 1904–1907), by L. P. Breckenridge and Paul Diserens. 1908. *Thirty cents.*

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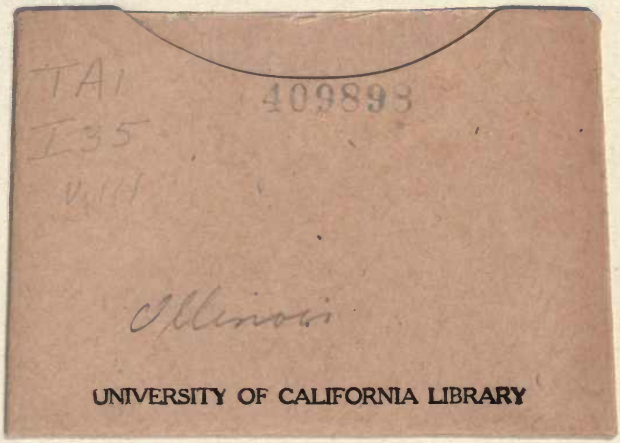
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